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### (54) A method for making positive printing plates from a heat mode sensitive imaging element

(57) According to the present invention there is provided a method for making lithographic printing plates including the following steps

- a) preparing a heat mode imaging element having on a lithographic base with a hydrophilic surface a first layer including a polymer, soluble in an aqueous alkaline solution and a top layer on the same side of the lithographic base as the first layer which top layer is sensitive to IR-radiation and is unpene- trable for an alkaline developer containing SiO<sub>2</sub> as silicates;
- b) exposing imagewise said heat mode imaging element to IR-radiation;
- c) developing said imagewise exposed heat mode imaging element with said alkaline developer so that the exposed areas of the top layer and the underlying areas of the first layer are dissolved and the unexposed areas of the first layer remain undis- solved characterized in that said top layer includes an IR-dye in an amount between 1 and 100% by weight of the total amount of said IR-sensitive top layer selected from the group consisting of indoaniline dyes, cyanine dyes, merocyanine dyes, oxonol dyes, porphine derivatives, anthraquinone dyes, merostyryl dyes, pyrylium compounds, diphe- nyl and triphenyl azo compounds and squarylium derivatives.

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## Description

## FIELD OF THE INVENTION

5 [0001] The present invention relates to a method for preparing a lithographic printing plate using a heat mode imaging element comprising an IR sensitive top layer.

More specifically the invention is related to a method for preparing a lithographic printing plate using a heat mode imaging element whereby the capacity of the top layer of being penetrated and/or solubilised by an aqueous developer is changed upon exposure.

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## BACKGROUND OF THE INVENTION

[0002] Lithography is the process of printing from specially prepared surfaces, some areas of which are capable of accepting lithographic ink, whereas other areas, when moistened with water, will not accept the ink. The areas which accept ink form the printing image areas and the ink-rejecting areas form the background areas.

15 [0003] In the art of photolithography, a photographic material is made imagewise receptive to oily or greasy inks in the photo-exposed (negative-working) or in the non-exposed areas (positive-working) on a hydrophilic background.

[0004] In the production of common lithographic printing plates, also called surface litho plates or planographic printing plates, a support that has affinity to water or obtains such affinity by chemical treatment is coated with a thin layer 20 of a photosensitive composition. Coatings for that purpose include light-sensitive polymer layers containing diazo compounds, dichromate-sensitized hydrophilic colloids and a large variety of synthetic photopolymers. Particularly diazo-sensitized systems are widely used.

[0005] Upon imagewise exposure of the light-sensitive layer the exposed image areas become insoluble and the unexposed areas remain soluble. The plate is then developed with a suitable liquid to remove the diazonium salt or diazo resin in the unexposed areas.

[0006] Alternatively, printing plates are known that include a photosensitive coating that upon image-wise exposure is rendered soluble at the exposed areas. Subsequent development then removes the exposed areas. A typical example of such photosensitive coating is a quinone-diazide based coating.

[0007] Typically, the above described photographic materials from which the printing plates are made are camera-exposed through a photographic film that contains the image that is to be reproduced in a lithographic printing process. Such method of working is cumbersome and labor intensive. However, on the other hand, the printing plates thus obtained are of superior lithographic quality.

[0008] Attempts have thus been made to eliminate the need for a photographic film in the above process and in particular to obtain a printing plate directly from computer data representing the image to be reproduced. However the photosensitive coating is not sensitive enough to be directly exposed with a laser. Therefor it has been proposed to coat a silver halide layer on top of the photosensitive coating. The silver halide can then directly be exposed by means of a laser under the control of a computer. Subsequently, the silver halide layer is developed leaving a silver image on top of the photosensitive coating. That silver image then serves as a mask in an overall exposure of the photosensitive coating. After the overall exposure the silver image is removed and the photosensitive coating is developed. Such method 40 is disclosed in for example JP-A- 60- 61 752 but has the disadvantage that a complex development and associated developing liquids are needed.

[0009] GB-1 492 070 discloses a method wherein a metal layer or a layer containing carbon black is provided on a photosensitive coating. This metal layer is then ablated by means of a laser so that an image mask on the photosensitive layer is obtained. The photosensitive layer is then overall exposed by UV-light through the image mask. After 45 removal of the image mask, the photosensitive layer is developed to obtain a printing plate. This method however still has the disadvantage that the image mask has to be removed prior to development of the photosensitive layer by a cumbersome processing.

[0010] Furthermore methods are known for making printing plates involving the use of imaging elements that are heat-sensitive rather than photosensitive. A particular disadvantage of photosensitive imaging elements such as 50 described above for making a printing plate is that they have to be shielded from the light. Furthermore they have a problem of sensitivity in view of the storage stability and they show a lower resolution. The trend towards heat mode printing plate precursors is clearly seen on the market.

[0011] For example, Research Disclosure no. 33303 of January 1992 discloses a heat mode imaging element comprising on a support a cross-linked hydrophilic layer containing thermoplastic polymer particles and an infrared absorbing pigment such as e.g. carbon black. By image-wise exposure to an infrared laser, the thermoplastic polymer particles 55 are image-wise coagulated thereby rendering the surface of the imaging element at these areas ink-acceptant without any further development. A disadvantage of this method is that the printing plate obtained is easily damaged since the non-printing areas may become ink accepting when some pressure is applied thereto. Moreover, under critical condi-

tions, the lithographic performance of such a printing plate may be poor and accordingly such printing plate has little lithographic printing latitude.

[0012] US-P- 4 708 925 discloses imaging elements including a photosensitive composition comprising an alkali-soluble novolac resin and an onium-salt. This composition can optionally contain an IR-sensitizer. After image-wise exposing said imaging element to UV - visible - or IR-radiation followed by a development step with an aqueous alkali liquid there is obtained a positive or negative working printing plate. The printing results of a lithographic plate obtained by irradiating and developing said imaging element are poor.

[0013] EP-A- 625 728 discloses an imaging element comprising a layer which is sensitive to UV- and IR-irradiation and which can be positive or negative working. This layer comprises a resole resin, a novolac resin, a latent Bronsted acid and an IR-absorbing substance. The printing results of a lithographic plate obtained by irradiating and developing said imaging element are poor.

[0014] US-P- 5 340 699 is almost identical with EP-A- 625 728 but discloses the method for obtaining a negative wording IR-laser recording imaging element. The IR-sensitive layer comprises a resole resin, a novolac resin, a latent Bronsted acid and an IR-absorbing substance. The printing results of a lithographic plate obtained by irradiating and developing said imaging element are poor.

[0015] Furthermore EP-A- 678 380 discloses a method wherein a protective layer is provided on a grained metal support underlying a laser-ablatable surface layer. Upon image-wise exposure the surface layer is fully ablated as well as some parts of the protective layer. The printing plate is then treated with a cleaning solution to remove the residu of the protective layer and thereby exposing the hydrophilic surface layer.

[0016] EP-A- 97 200 588.8 discloses a heat mode imaging element for making lithographic printing plates comprising on a lithographic base having a hydrophilic surface an intermediate layer comprising a polymer, soluble in an aqueous alkaline solution and a top layer that is sensitive to IR-radiation wherein said top layer upon exposure to IR-radiation has a decreased or increased capacity for being penetrated and/or solubilised by an aqueous alkaline solution.

[0017] Said heat-mode imaging element has the disadvantage that some ablation occurs during the irradiation causing formation of some debris. Said debris can interfere with the transmission of the laser beam ( e.g. by depositing on a focusing lens or as an aerosol that partially blocks transmission) or with the transport of the imaging element during or after recording when this debris remains loosely adhered to the plate and deposition of said debris occurs on the transport rollers.

[0018] GB-A-1 245 924 discloses an information recording method wherein a recording material is used comprising a heat-sensitive recording layer of a composition such that the solubility of any given area of the layer in a given solvent can be increased by heating that area of the layer, wherein the said layer is information-wise heated to produce a record of the information in terms of a difference in the solubilities in the said solvent of different areas of the recording layer, and wherein the whole layer is then contacted with such solvent to cause the portions of the recording layer which are soluble or most soluble in such solvent to be removed or penetrated by such solvent.

[0019] EP-A-347 245 discloses a method for development-processing of presensitized plates for use in making lithographic printing plates which comprises imagewise exposing the presensitized plate to light and development-processing the exposed presensitized plate with an alkaline developer and a replenisher, wherein the developer and the replenisher are aqueous solutions of an alkali metal silicate and the ratio  $(\text{SiO}_2):(\text{M}_2\text{O})$  (wherein  $(\text{SiO}_2)$  and  $(\text{M}_2\text{O})$  are the molar concentrations of respectively  $\text{SiO}_2$  and an alkali metal oxide  $\text{M}_2\text{O}$ ) of the replenisher ranges from 0.6 to 1.5.

[0020] EP-A- 732 628 discloses an aqueous alkaline developing solution comprising an alkaline composition of at least one compound selected from the group consisting of alkali metal silicate and alkali metal metasilicate, wherein the  $\text{M}_2\text{O}/\text{SiO}_2$  molar ratio of said alkaline mixture is in the range from 0.5 to 1.2, the total content of said alkaline mixture being in the range of from 5 to 15 % by weight of total developing solution, and wherein said developing solution comprises a non-ionic surfactant and at least another surfactant selected from the group consisting of anionic surfactants and amphoteric surfactants.

[0021] US-P- 5 466 557 discloses a radiation-sensitive composition comprising (1) a resole resin, (2) a novolac resin, (3) a latent Bronsted acid, (4) an infrared absorber, and (5) terephthalaldehyde.

[0022] GB-A- 1 155 035 discloses a method of recording information, wherein a recording material is used comprising a layer of a polymeric material which when any given area of the layer is sufficiently heated undergoes in that area a modification resulting in a decrease in the solubility of that area of the layer in water or an aqueous medium, such layer also incorporating a substance or substances distributed over the whole area of the layer and being capable of being heated by exposing the layer to intense radiant energy which is absorbed by such substance or substances, and wherein the said material is exposed to intense radiant energy which is distributed over the material in a pattern determined by the information to be recorded and which is at least partly absorbed by said distributed substance or substances, so that a corresponding heat pattern is generated in the material, whereby such information is recorded in terms of a difference in the solubilities in water or an aqueous medium of different areas of said layer.

[0023] GB-A- 1 154 568 discloses a method of recording a graphic original having contrasting light-absorbing and light-transmitting areas, wherein a recording material comprising a supported layer composed mainly of gelatin the

water-solubility or water-absorptive capacity of which increases if the layer is sufficiently heated, such layer also having light absorbing substance(s) distributed therein, is placed with such gelatin layer in contact with the light-absorbing areas of the original and the said gelatin layer is exposed to light through the original, the intensity of the light and the duration of the exposure being such that the areas of the gelatin layer in contact with the light-absorbing areas of the original are substantially unaffected by heat conduction from such light-absorbing areas, but the water-solubility or water-absorptive capacity of the other areas of the gelatin layer is increased by heating thereof due to absorption of copying light by the light-absorbing substance(s) in those other areas of the gelatin layer.

5 [0024] So, there is a need for a heat-mode imaging element which undergoes no ablation during the IR-radiation.

10 OBJECTS OF THE INVENTION

[0025] It is an object of the invention to provide a method for making lithographic printing plates, using a heat mode imaging element which undergoes no ablation during the IR-radiation.

15 [0026] It is another object of the invention to provide a method for making positive lithographic printing plates from a heat mode sensitive imaging element having excellent printing properties, developable in a selective, rapid convenient and ecological way.

[0027] It is further an object of the present invention to provide a method for making positive lithographic printing plates from a heat mode sensitive imaging element having a high infrared sensitivity.

20 [0028] It is also an object of the present invention to provide a method for making positive lithographic printing plates from a heat mode sensitive imaging element which can be imaged by laser exposure at short as well as at long pixel dwell times.

[0029] Further objects of the present invention will become clear from the description hereinafter.

25 SUMMARY OF THE INVENTION

[0030] According to the present invention there is provided a method for making lithographic printing plates including the following steps

30 a) preparing a heat mode imaging element having on a lithographic base with a hydrophilic surface a first layer including a polymer, soluble in an aqueous alkaline solution and a top layer on the same side of the lithographic base as the first layer which top layer is sensitive to IR-radiation and is unpenetrable for an alkaline developer containing  $\text{SiO}_2$  as silicates;

b) exposing imagewise said heat mode imaging element to IR-radiation;

35 c) developing said imagewise exposed heat mode imaging element with said alkaline developer so that the exposed areas of the top layer and the underlying areas of the first layer are dissolved and the unexposed areas of the first layer remain undissolved characterized in that said top layer includes an IR-dye in an amount between 1 and 100% by weight of the total amount of said IR-sensitive top layer selected from the group consisting of indoaniline dyes, cyanine dyes, merocyanine dyes, oxonol dyes, porphine derivatives, anthraquinone dyes, merostyryl dyes, pyrylium compounds, diphenyl and triphenyl azo compounds and squarylium derivatives.

40 DETAILED DESCRIPTION OF THE INVENTION

[0031] It has been found that according to the present invention, using a heat-sensitive imaging element as described above, lithographic printing plates of high quality can be obtained without ablation in an ecologically acceptable way.

45 [0032] Preferably a method according to the invention for making lithographic printing plates including the following steps

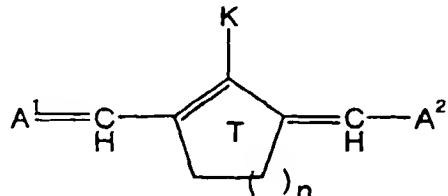
50 a) preparing a heat mode imaging element having on a lithographic base with a hydrophilic surface a first layer including a polymer, soluble in an aqueous alkaline solution and a top layer on the same side of the lithographic base as the first layer which top layer consists of a binder resin, is sensitive to IR-radiation and is unpenetrable for an alkaline developer containing  $\text{SiO}_2$  as silicate;

b) exposing imagewise said heat mode imaging element to IR-radiation;

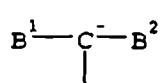
55 c) developing said imagewise exposed heat mode imaging element with said alkaline developer so that the exposed areas of the top layer and the underlying areas of the first layer are dissolved and the unexposed areas of the first layer remain undissolved characterized in that said top layer includes an IR-dye in an amount between 1 and 100% by weight of the total amount of said IR-sensitive top layer.

[0033] The top layer, in accordance with the present invention consists of an IR-dye and preferably of an IR-dye and

5 a binder resin. A mixture of IR-dyes may be used, but it is preferred to use only one IR-dye. Suitable IR-dyes are known since a long time and belong to several different chemical classes, e.g. indoaniline dyes, oxonol dyes, porphine derivatives, anthraquinone dyes, merostyryl dyes, pyrylium compounds and sqarylium derivatives. Preferably said IR-dyes, especially for irradiation with a laser source with an emission spectrum of about 1060 nm belongs to the scope of the general formula of the German patent application DE- 4. 31 162. This general formula (I) is represented by :



wherein K represents Q together with a counterion An-, or



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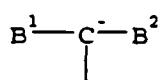
wherein Q represents chlorine, fluorine, bromine, iodine, alkyloxy, aryloxy, dialkylamino, diarylamino, alkylarylamino, nitro, cyano, alkylsulphonyl, arylsulphonyl, heterocyclyl, or a moiety represented by L-S-,

30 wherein L represents alkyl, aryl, heterocyclyl, cyano or substituted carbonyl, thiocarbonyl or iminocarbonyl,

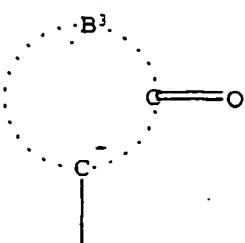
An- represents an anion commonly used in the chemistry of cationic dyes, or an equivalent thereof,

35 B<sup>1</sup> represents cyano, alkoxy carbonyl, alkyl- or aryl carbonyl, or aminocarbonyl optionally substituted once or twice at the nitrogen atom by alkyl and/or aryl,

B<sup>2</sup> represents arylsulphonyl, alkylsulphonyl, heteroaryl, or,



can be represented by



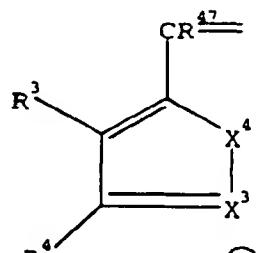
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wherein B<sup>3</sup> represents the non-metal atoms to complete a carbocyclic or heterocyclic ring,

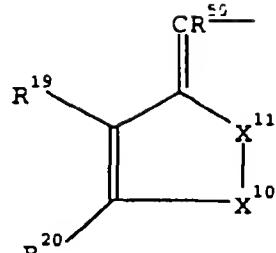
ring T can be substituted by 1 to 3 C<sub>1</sub> - C<sub>4</sub> alkyl groups, n = 1 or 2,

and A<sup>1</sup> and A<sup>2</sup> can represent following combinations :

5 (1) moieties of formulas (IIIa) and (IIIb) :



(IIIa)



(IIIb)

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wherein X<sup>3</sup>, X<sup>10</sup> = O,  
X<sup>4</sup>, X<sup>11</sup> = -CR<sup>38</sup> = -CR<sup>39</sup>,

25 R<sup>38</sup> and R<sup>39</sup> each independently represent hydrogen, alkyl, aryl or together the necessary non-metal atoms to complete a cycloaliphatic, aromatic or heterocyclic 5- or 7-membered ring, or independently from each other, the necessary non-metal atoms to complete a cycloaliphatic, aromatic or heterocyclic 5- or 7-membered ring, and R<sup>3</sup>, R<sup>4</sup>, R<sup>19</sup> and R<sup>20</sup> each independently represent hydrogen, C<sub>1</sub> - C<sub>8</sub> alkyl, aryl, halogen, cyano, alkoxy-carbonyl, optionally substituted aminocarbonyl, amino, monoalkylamino, dialkylamino, hydroxy, alkoxy, aryloxy, alkylthio, arylthio, acyloxy, acylamino, arylamino, alkylcarbonyl, arylcarbonyl, or the necessary non-metal atoms to complete a cycloaliphatic, aromatic or heterocyclic 5- or 7-membered ring.

30 R<sup>47</sup> and R<sup>50</sup> each independently represent hydrogen, alkyl, aryl, cyano, alkoxy-cyano or the non-metal atoms to form a saturated or unsaturated 5- to 7-membered ring, in the first case between R<sup>47</sup> and resp. X<sup>4</sup> and R<sup>3</sup>, in the second case between R<sup>50</sup> and resp. X<sup>11</sup> and R<sup>19</sup>.

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(2) moieties of the same formulas (IIIa) and (IIIb)

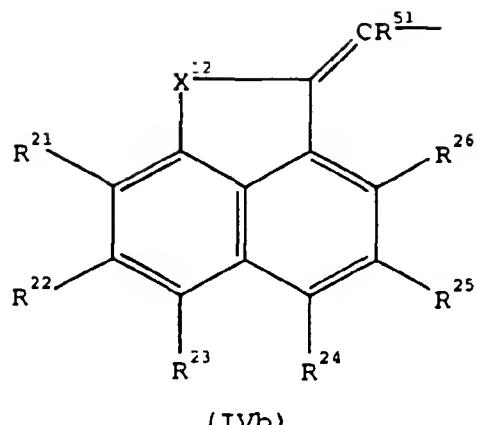
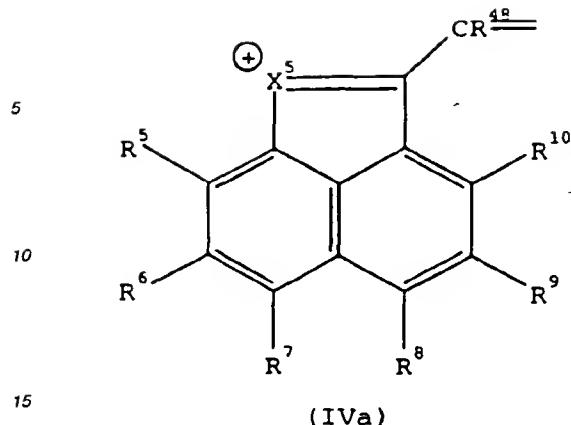
wherein X<sup>3</sup>, X<sup>10</sup> = R<sup>44</sup>N,  
X<sup>4</sup>, X<sup>11</sup> = -CR<sup>38</sup> = -CR<sup>39</sup>,

40 and wherein R<sup>3</sup> and R<sup>4</sup>, respectively R<sup>38</sup> and R<sup>39</sup> together represent the atoms to complete an optionally substituted aromatic ring,  
and wherein R<sup>44</sup> represents optionally substituted alkyl or aryl, or the necessary atoms to complete a 5- or 7-membered ring.

45 (3) moieties of the formulas (IVa) and (IVb) :

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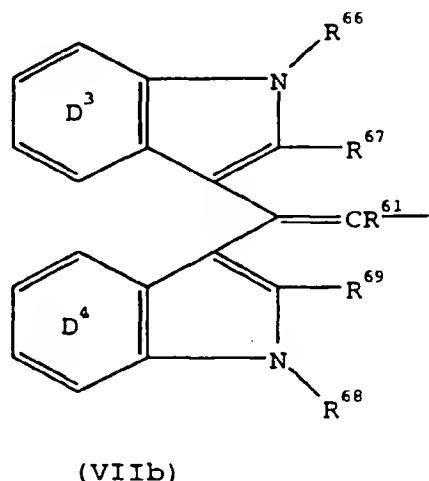
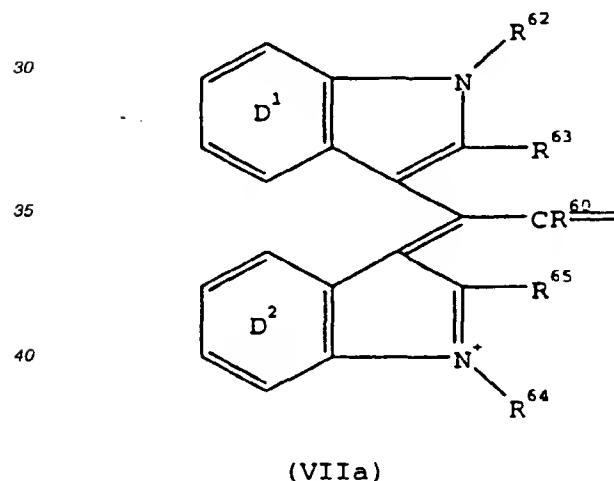


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wherein X<sup>5</sup> and X<sup>12</sup> each independently represent O, S, Se, Te or R<sup>44</sup>N,  
 R<sup>5</sup> to R<sup>10</sup> and R<sup>21</sup> to R<sup>26</sup> each independently represent one of the meanings given above for R<sup>3</sup>,  
 and R<sup>48</sup> and R<sup>51</sup> each independently represent hydrogen, alkyl, aryl or alkoxy carbonyl,  
 with the exception for those compounds in which together X<sup>5</sup>, X<sup>12</sup> = R<sup>44</sup>N and Q = halogen.

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(4) moieties of formulas (VIIa) and (VIIb)

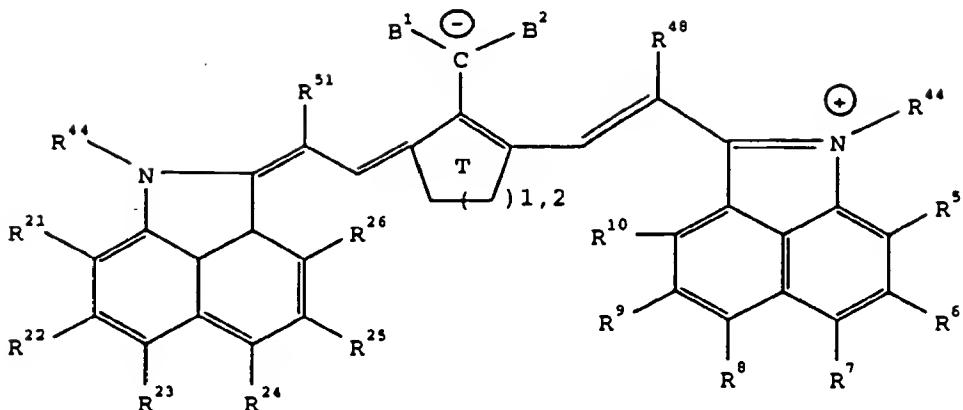


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wherein R<sup>60</sup> and R<sup>61</sup> each independently represent hydrogen, alkyl, aryl, cyano, alkoxy carbonyl, halogen,  
 R<sup>62</sup>, R<sup>64</sup>, R<sup>66</sup>, R<sup>68</sup> each independently represent alkyl or aryl,  
 R<sup>63</sup>, R<sup>65</sup>, R<sup>67</sup>, R<sup>69</sup> each independently represent hydrogen, alkyl or aryl,  
 and wherein the rings D<sup>1</sup> to D<sup>4</sup> each independently can be substituted once or frequently by hydrogen, chlorine, bromine, alkyl, or alkoxy.

55 [0034] Most preferred subclasses of this general formula (I) are the following :

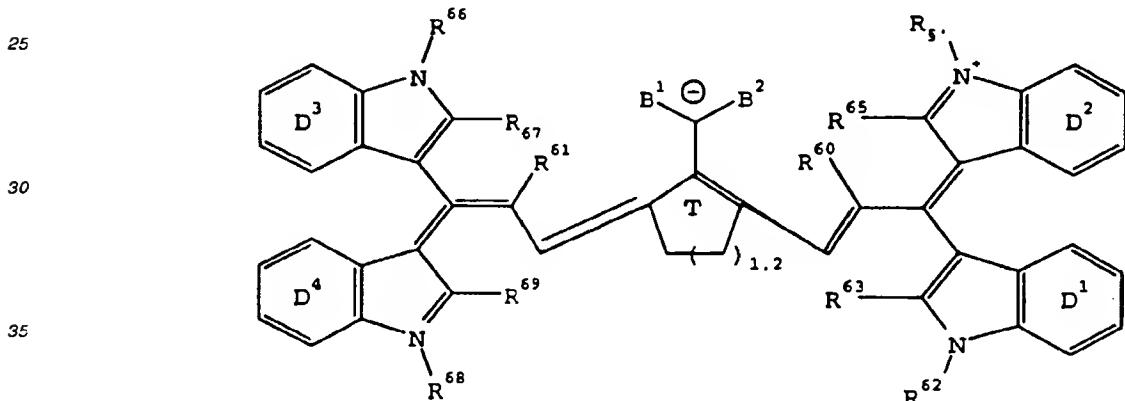
- compounds according to formula (XXI)



(XXI)

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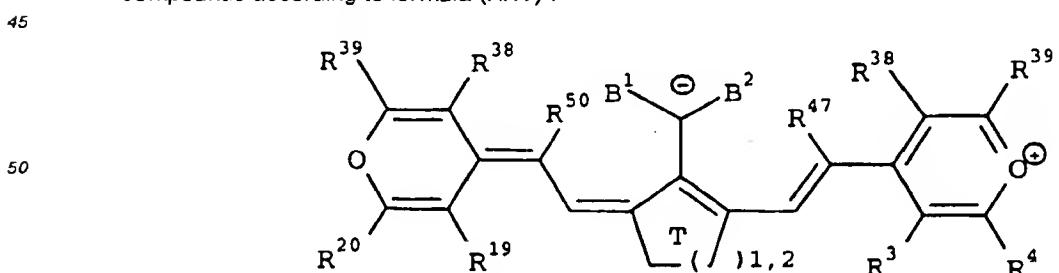
- compounds according to formula (XXIII) :



(XXIII)

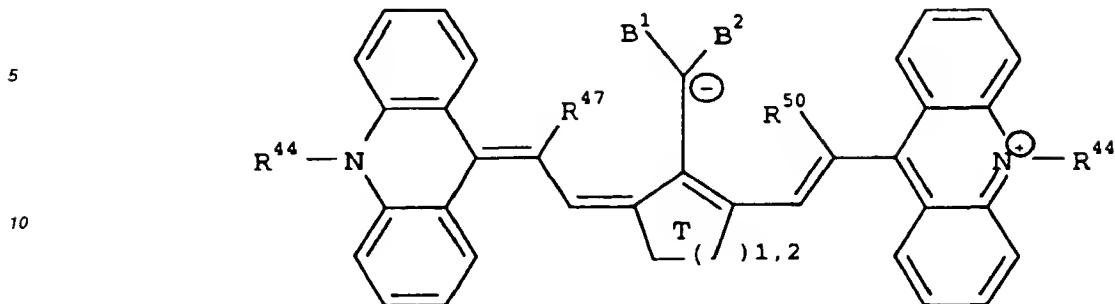
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- compounds according to formula (XXV) :



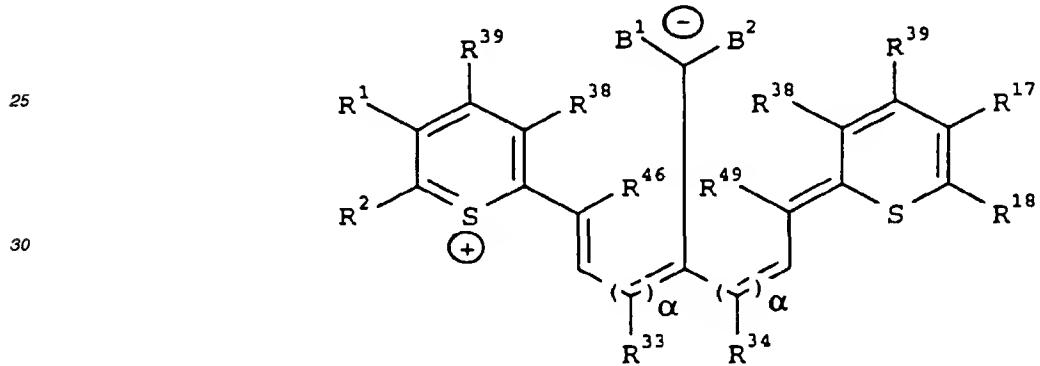
(XXV)

5 - compounds according to formula (XXVII)



(XXVII)

20 - compounds according to formula (XXIX) :



(XXIX)

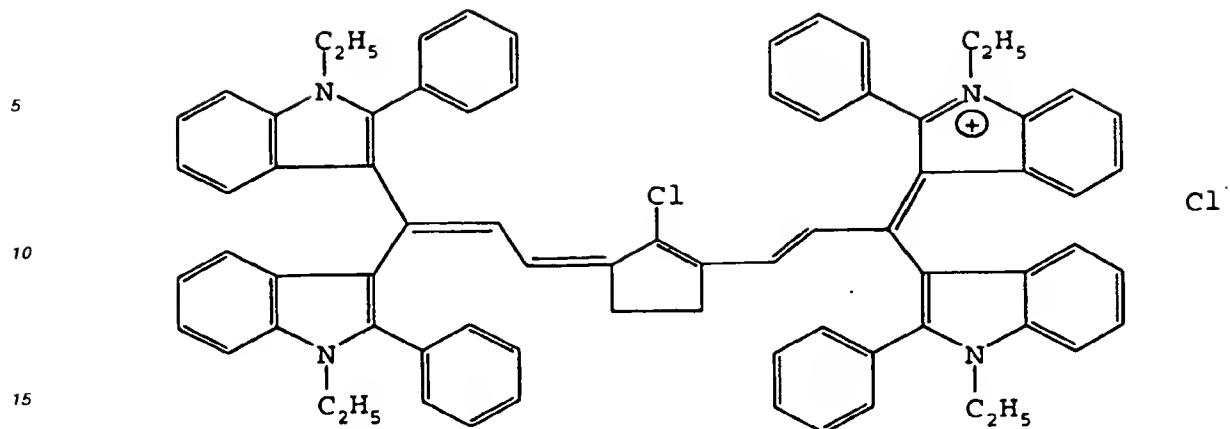
40 [0035] In the formulas of these subclasses R1, R2, R17 and R18 have the same meaning as R3, and B1, B2, the other R symbols, T, and the D symbols are defined as hereinbefore, and  $\alpha$  is 0 or 1.

[0036] Some specific infra-red absorbing dyes (IRD) corresponding to general formula (I) or to one of the preferred subclasses defined above which are chosen for the determination of specific spectral characteristics are listed below.

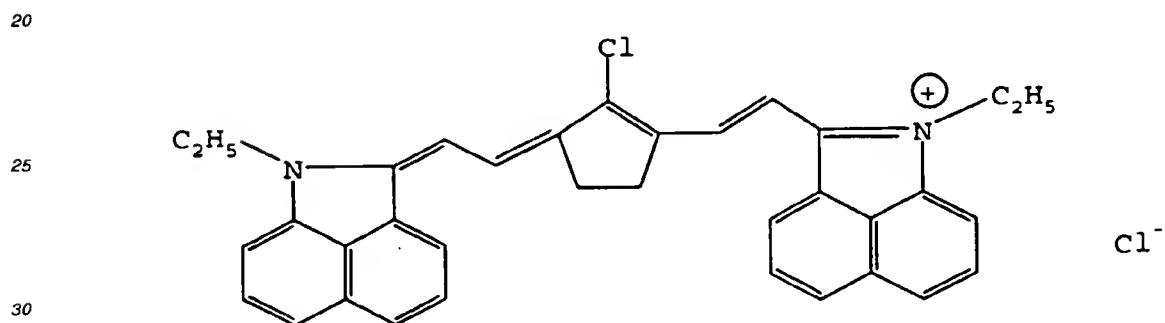
45 A reference number is designated to them by which they will be identified in the tables furtheron of the description and examples :

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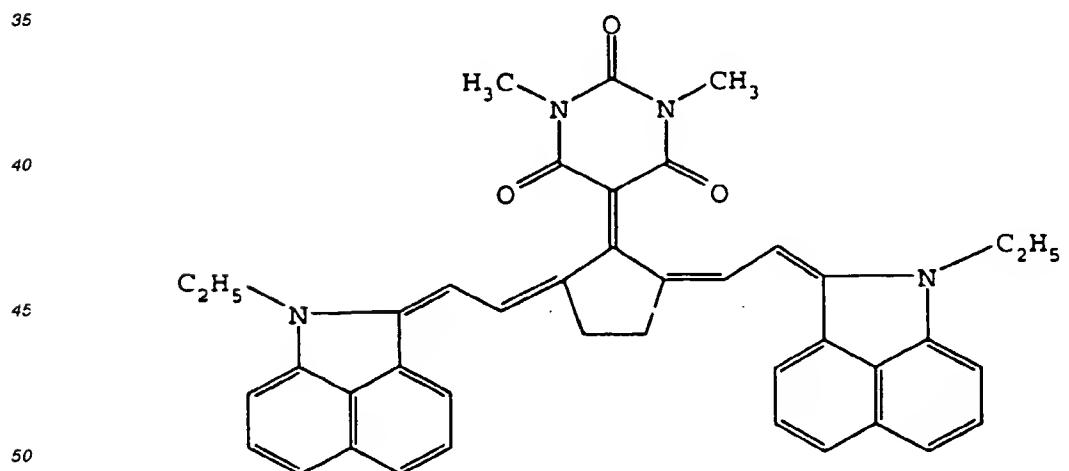
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IRD No. 1



IRD No. 2



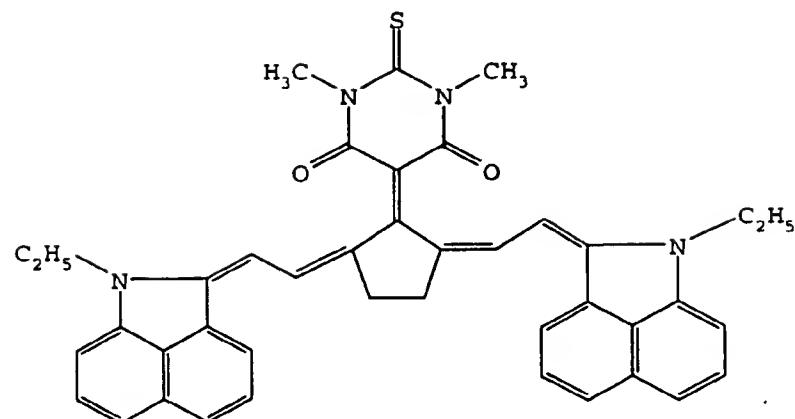
IRD No. 3

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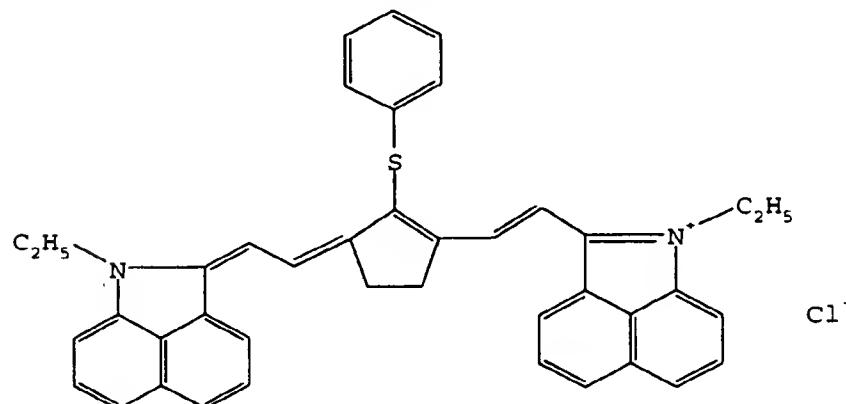


IRD No. 4

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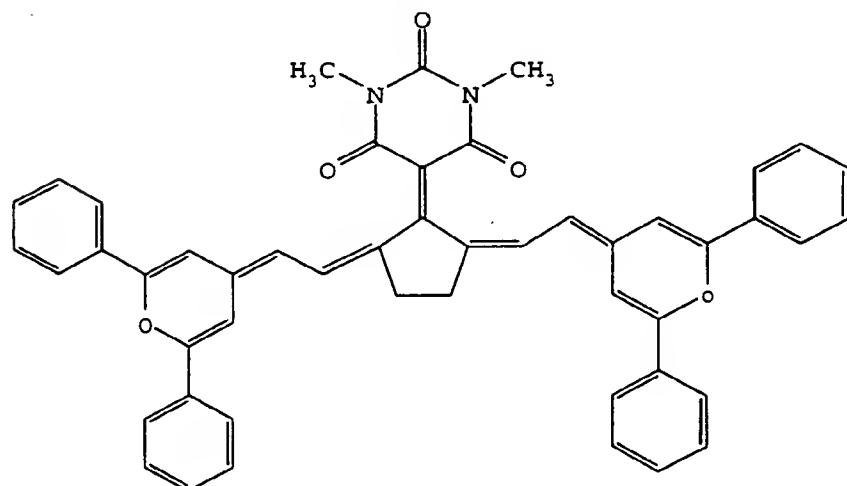
IRD No. 5

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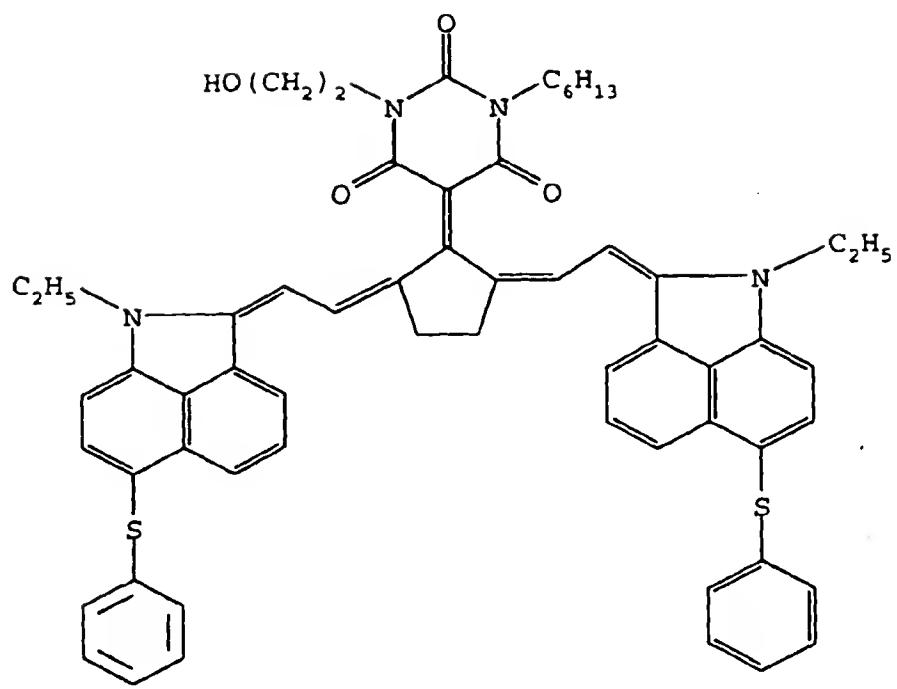
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IRD No. 6

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IRD No. 7

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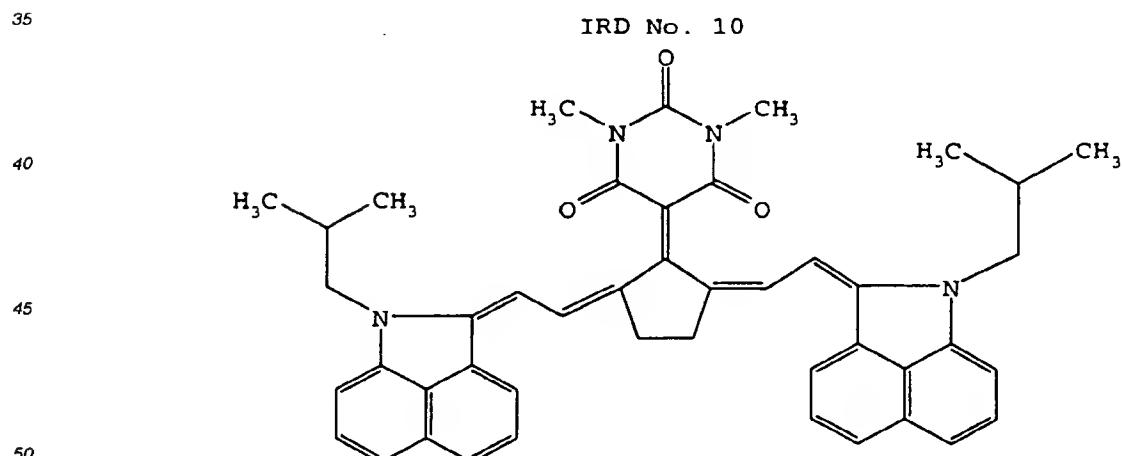
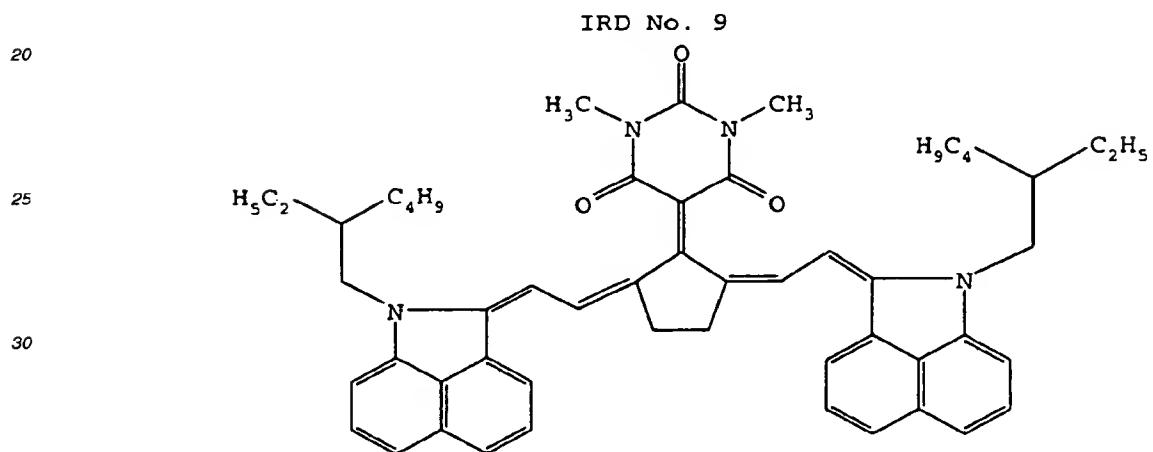
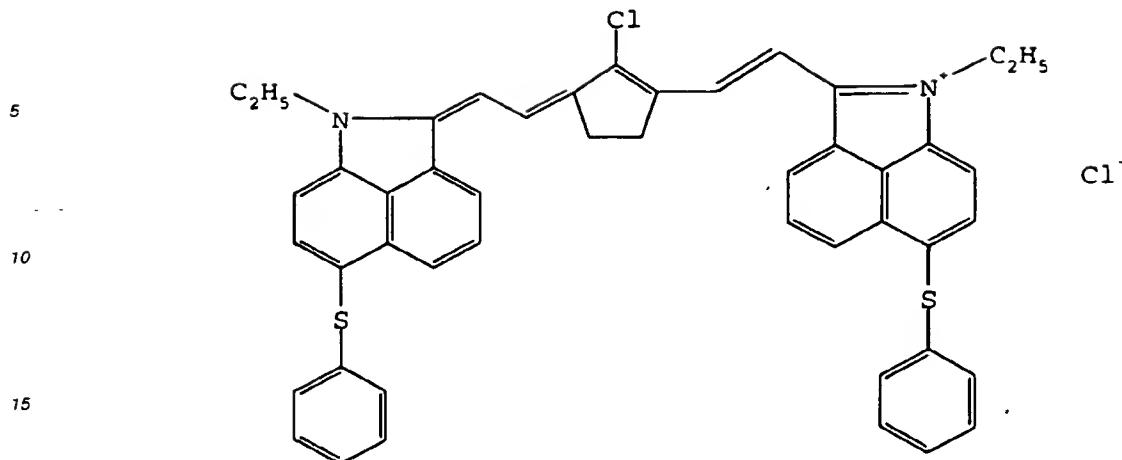
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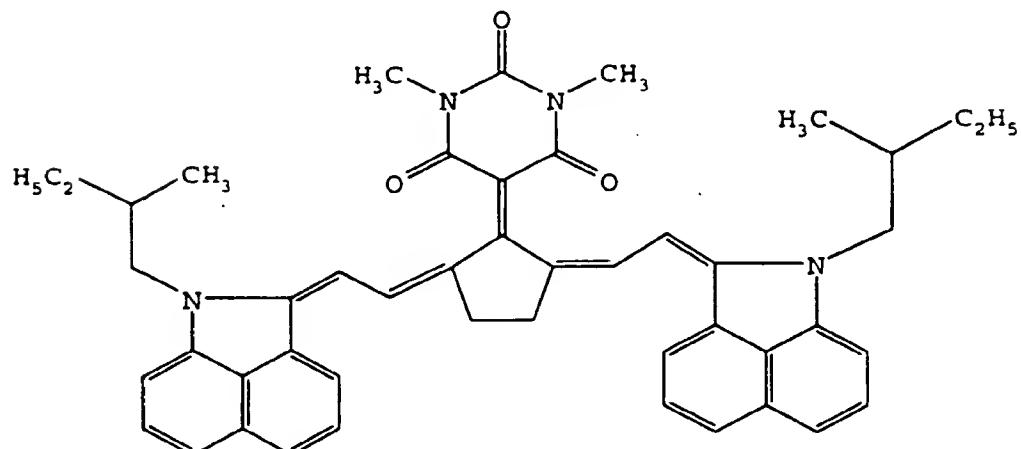
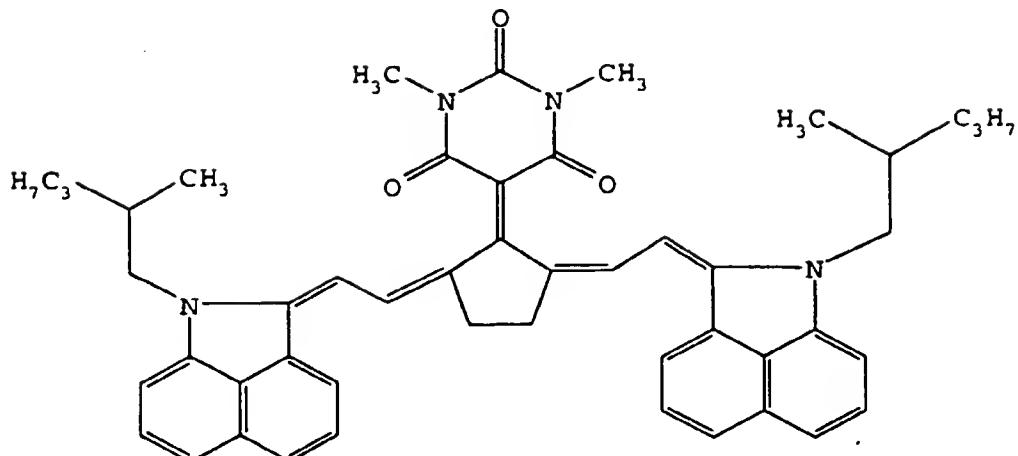
IRD No. 8

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IRD No. 11

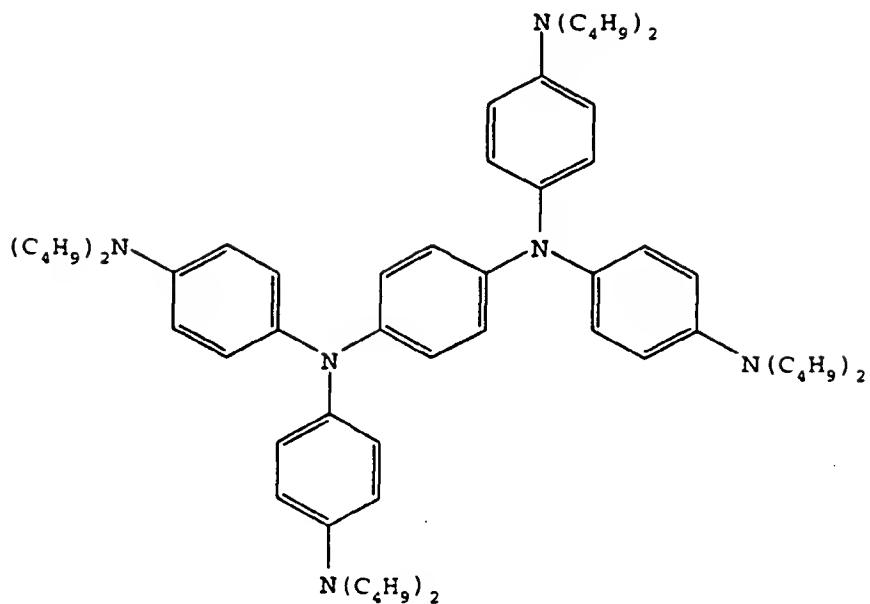


[0037] Further suitable prior art dyes included in the experimental investigation of spectral parameters are represented by following formulas :

[0038] IRD-14 is a commercial product known as CYASORB IR165, marketed by American Cyanamid Co, Glendale Protective Technologie Division, Woodbury, New-York. It is a mixture of two parts of the molecular non-ionic form (IRD-14a) and three parts of the ionic form (IRD-14b) represented by :

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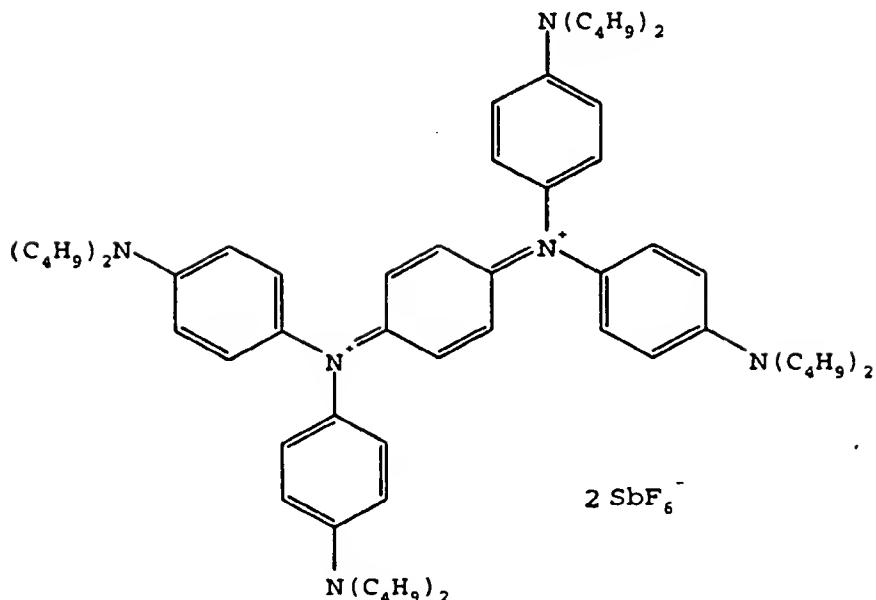
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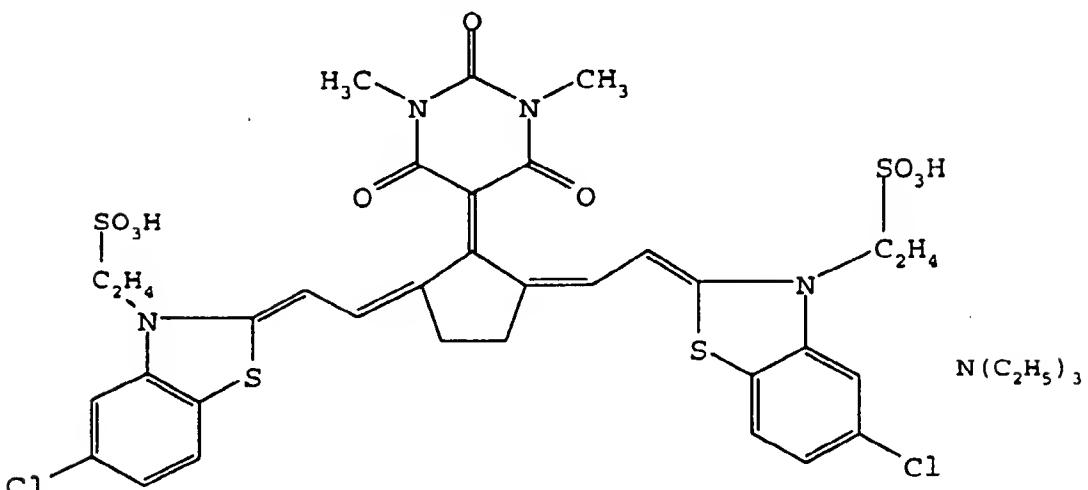
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IRD No. 14b



IRD No. 15

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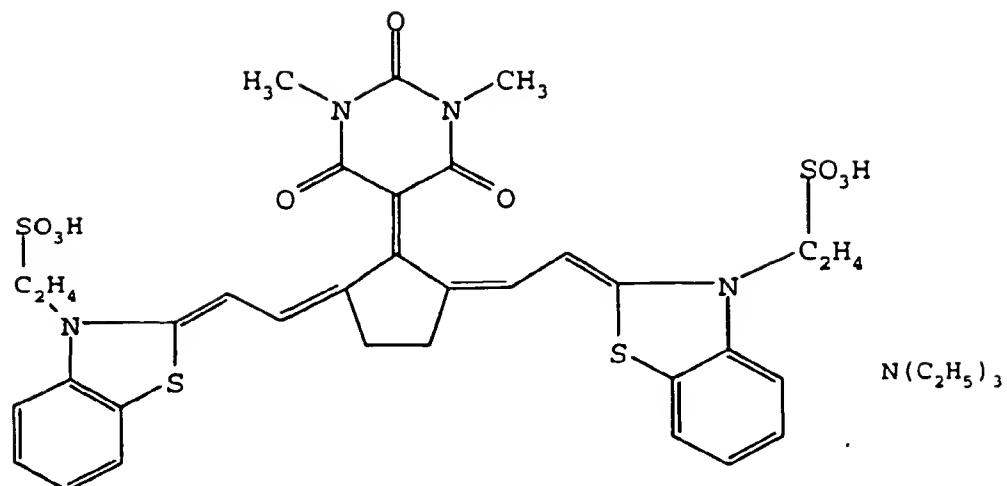
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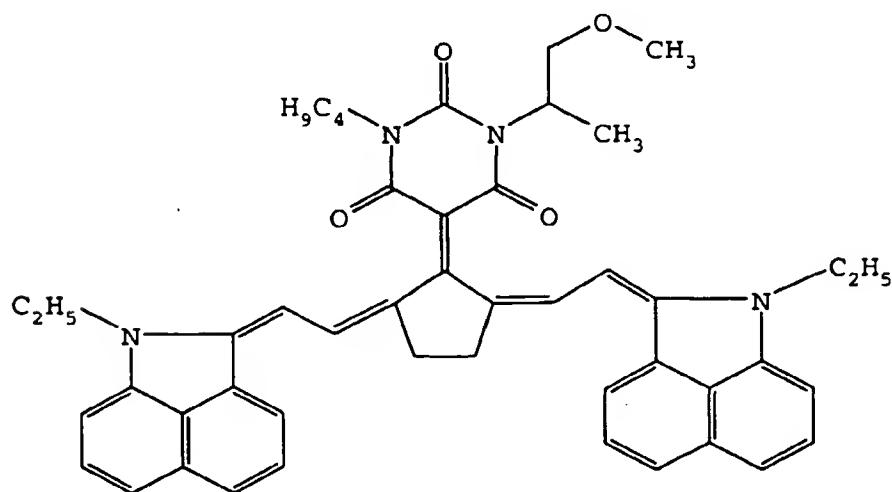
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IRD No. 16

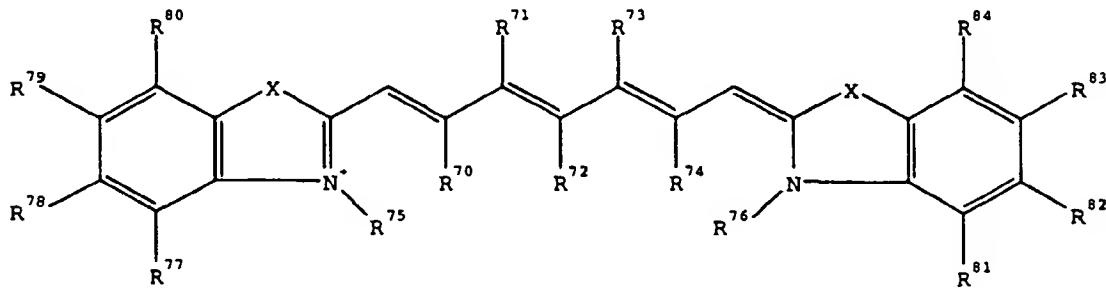


IRD No. 17

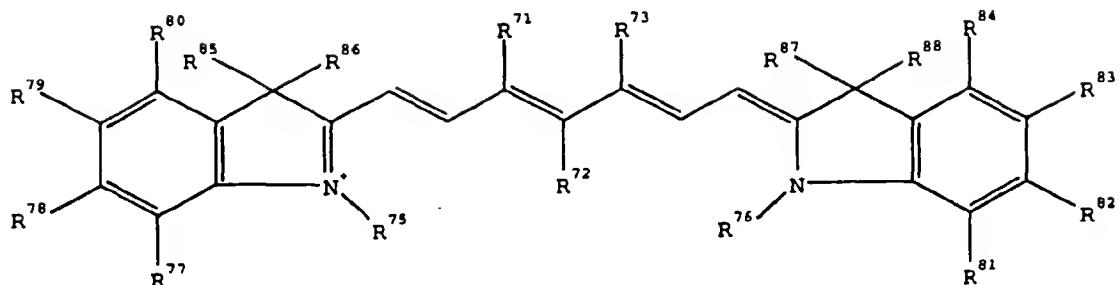
[0039] Other preferred IR-dyes, especially for irradiation with a laser source with an emission spectrum of about 830 nm belong to the scope of the following general formulas.

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wherein X, X' each independently represents O, S

R<sup>70</sup>-R<sup>74</sup> each independently may represent hydrogen, alkyl or aryl; R<sup>70</sup> together with R<sup>72</sup>, R<sup>72</sup> together with R<sup>74</sup>, R<sup>71</sup> together with R<sup>73</sup>, R<sup>70</sup> together with R<sup>72</sup> and R<sup>74</sup> may form a carbocyclic ring.

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R<sup>72</sup> may also represent halogen, NR<sup>88</sup>R<sup>89</sup> (R<sup>88</sup>, R<sup>89</sup> each independently represents alkyl, aryl, or may form a (hetero)cyclic ring), PR<sup>88</sup>R<sup>89</sup>, ester-COOR<sup>92</sup> (R<sup>92</sup> represents alkyl, or aryl), barbituric acid group (with optionally substituted N-atoms).

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R<sup>71</sup> or R<sup>73</sup> may represent: -OCOR<sup>93</sup>; R<sup>93</sup> represents alkyl, or aryl. R<sup>77</sup> together with R<sup>78</sup>, R<sup>78</sup> together with R<sup>79</sup>, R<sup>79</sup> together with R<sup>80</sup>, R<sup>81</sup> together with R<sup>82</sup>, R<sup>82</sup> together with R<sup>83</sup>, R<sup>83</sup> together with R<sup>84</sup> may form an annulated benzoring optionally substituted with a carbocyclic acid, ester or sulphogroup.

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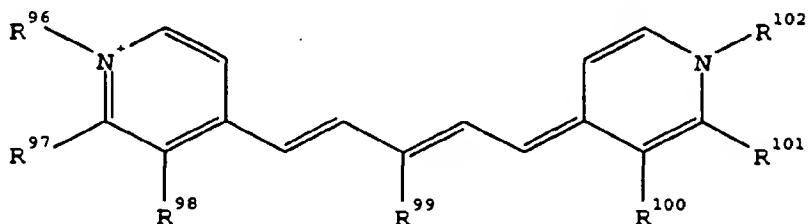
R<sup>78</sup>, R<sup>79</sup>, R<sup>82</sup>, R<sup>83</sup> each independently may represent hydrogen, alkyl, aryl, halogen, ester, carbocyclic acid, amide, amine, nitrile, alkoxy, aryloxy, or sulpho group.

R<sup>85</sup>, R<sup>86</sup>, R<sup>87</sup>, R<sup>88</sup> each independently may represent an alkyl group, R<sup>85</sup> together with R<sup>86</sup>, R<sup>87</sup> together with R<sup>88</sup> may form a cyclic (spiro)ring.

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R<sup>75</sup>, R<sup>76</sup> each independently represents an alkyl, aryl group; -C<sub>n</sub>H<sub>2n</sub>SO<sub>3</sub>M (n represents an integer from 2 to 4 and M H or positively charged counterion); -C<sub>n</sub>H<sub>2n</sub>COOM (n represents an integer from 1 to 5 and M H or positively charged counterion); -C<sub>n</sub>H<sub>2n</sub>COOR<sup>94</sup> (n represents an integer from 1 to 5 and R<sup>94</sup> alkyl, or aryl group); -L1-CONHSO<sub>2</sub>R<sup>95</sup> (L1 represents -C<sub>n</sub>H<sub>2n</sub>- with n an integer from 1 to 4 and R<sup>95</sup> alkyl or aryl).

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R<sup>96</sup>, R<sup>102</sup> represents alkyl, or aryl group; -C<sub>n</sub>H<sub>2n</sub>SO<sub>3</sub>M (n represents an integer from 2 to 4 and M H or positively charged counterion); -C<sub>n</sub>H<sub>2n</sub>COOM (n represents an integer from 1 to 5 and M H or positively charged counterion); -C<sub>n</sub>H<sub>2n</sub>COOR<sup>103</sup> (n represents an integer from 1 to 5 and R<sup>103</sup> alkyl, or aryl group); -L1-CONHSO<sub>2</sub>R<sup>104</sup> (L1 represents -C<sub>n</sub>H<sub>2n</sub>- with n an integer from 1 to 4 and R<sup>104</sup> alkyl or aryl).

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R<sup>97</sup>, R<sup>98</sup>, R<sup>100</sup>, R<sup>101</sup> may each independently represent: hydrogen, alkyl, aryl; R<sup>97</sup> together with R<sup>98</sup>, R<sup>100</sup> together with R<sup>101</sup> may form an annulated benzoring.

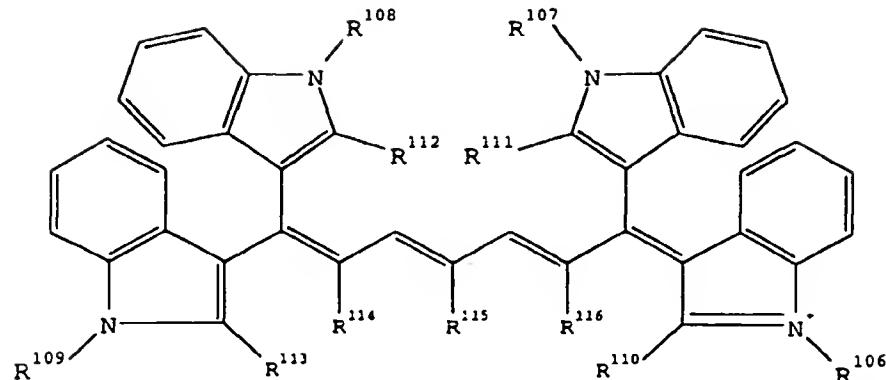
R<sup>98</sup> may represent: hydrogen, alkyl, aryl, halogen, ester, or -SO<sub>2</sub>R<sup>105</sup> (R<sup>105</sup> represents an alkyl or aryl).

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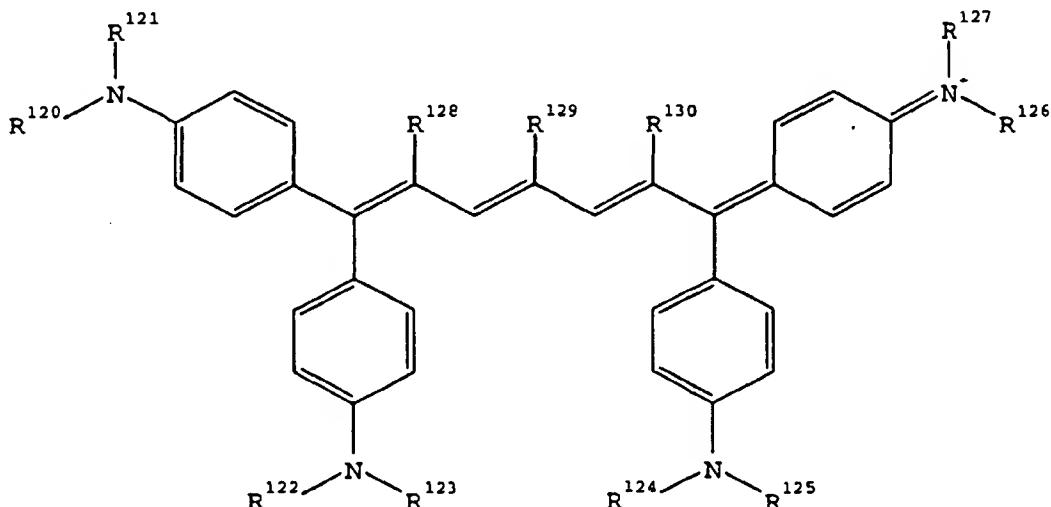
20  $R^{106}, R^{107}, R^{108}, R^{109}$  each independently may represent alkyl, aryl group;  $-C_nH_{2n}SO_3M$  represents an integer from 2 to 4 and M H or positively charged counterion);  $-C_nH_{2n}COOM$  (n represents an integer from 1 to 5 and M H or positively charged counterion);  $-C_nH_{2n}COOR^{117}$  (n represents an integer from 1 to 5 and  $R^{117}$  alkyl, or aryl group);  $-L1-CONHSO_2R^{118}$  (L1 represents  $-C_nH_{2n}-$  with n an integer from 1 to 4 and  $R^{118}$  alkyl or aryl).  
 25  $R^{110}, R^{111}, R^{112}, R^{113}$  each independently represents : hydrogen, alkyl, or aryl group.  
 $R^{114}, R^{115}, R^{116}$  each independently may represent : hydrogen, alkyl, or aryl group;  $R^{115}$  represents halogen, ester, or  $-SO_2R^{119}$  ( $R^{119}$  represents alkyl, or aryl).

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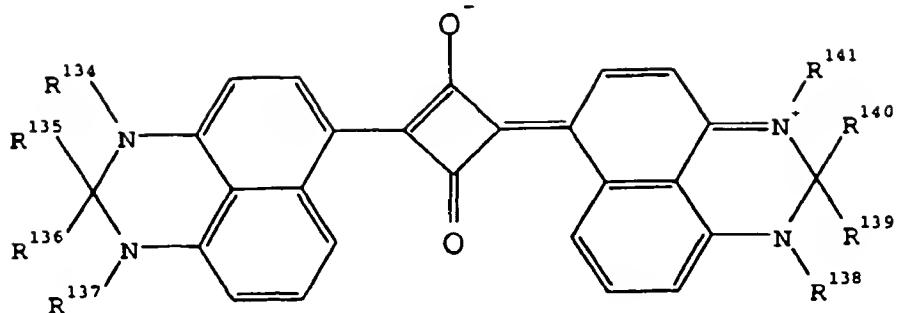
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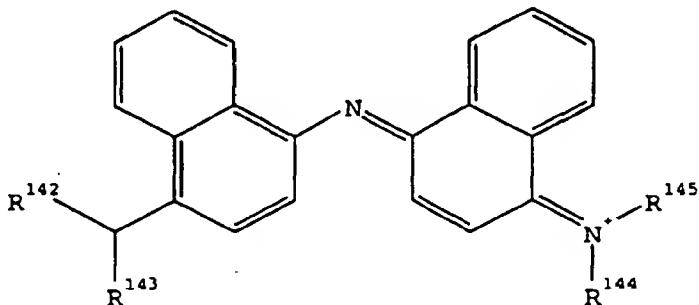
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50  $R^{120}, R^{121}, R^{122}, R^{123}, R^{124}, R^{125}, R^{126}, R^{127}$ : each independently may represent alkyl, aryl group;  $-C_nH_{2n}SO_3M$  (n represents an integer from 2 to 4 and M H or positively charged counterion);  $-C_nH_{2n}COOM$  (n represents an integer from 1 to 5 and M H or positively charged counterion);  $-C_nH_{2n}COOR^{131}$  (n represents an integer from 1 to 5 and  $R^{131}$  alkyl, or aryl group);  $-L1-CONHSO_2R^{132}$  (L1 represents  $-C_nH_{2n}-$  with n an integer from 1 to 4 and  $R^{132}$  alkyl or aryl).  
 55  $R^{120}$  together with  $R^{121}$ ,  $R^{122}$  together with  $R^{123}$ ,  $R^{124}$  together with  $R^{125}$ ,  $R^{126}$  together with  $R^{127}$  may form a cyclic ring.  
 $R^{128}, R^{129}, R^{130}$ : each independently may represents hydrogen, alkyl, or aryl group;  $R^{129}$  may represent : halogen, ester, or  $-SO_2R^{133}$  ( $R^{133}$  represents alkyl, or aryl).



15 R<sup>134</sup>, R<sup>137</sup>, R<sup>138</sup>, R<sup>141</sup> each independently may represent : hydrogen, alkyl, or aryl  
 R<sup>134</sup> together with R<sup>135</sup>, R<sup>141</sup> together with R<sup>140</sup> may form a carbocyclic ring.  
 R<sup>135</sup> together with R<sup>136</sup>, R<sup>139</sup> together with R<sup>140</sup> may form a carbocyclic ring.  
 R<sup>135</sup>, R<sup>136</sup>, R<sup>139</sup>, R<sup>140</sup> each independently may represent: hydrogen, alkyl, aryl group; - C<sub>n</sub>H<sub>2n</sub>SO<sub>3</sub>M (n represents an integer from 2 to 4 and M H or positively charged counterion); - C<sub>n</sub>H<sub>2n</sub>COOM (n represents an integer from 1 to 5 and M H or positively charged counterion);



35  $R^{142}, R^{143}, R^{144}, R^{145}$  each independently represents alkyl, aryl group;  $-C_nH_{2n}SO_3M$  represents an integer from 2 to 4 and M H or positively charged counterion);;  $-C_nH_{2n}COOM$  (n represents an integer from 1 to 5 and M H or positively charged counterion);  $-C_nH_{2n}COOR^{146}$  (n represents an integer from 1 to 5 and  $R^{146}$  alkyl, or aryl group);  $-L1-CONHSO_2R^{147}$  (L1 represents  $-C_nH_{2n}-$  with n an integer from 1 to 4 and  $R^{147}$  alkyl or aryl).  
 40 R142 together with R143, R144 together with R145 may form a cyclic ring.

The charge of the dyes can be compensated by any (intermolecular or intramolecular) counterion.

[0040] As a binder resin in the top layer gelatin, cellulose, cellulose esters e.g. cellulose acetate, polyvinyl alcohol, polyvinyl pyrrolidone, a copolymer of vinylidene chloride and acrylonitrile, poly(meth)acrylates, polyvinyl chloride, nitro-cellulose, silicone resins etc. can be used. Preferred as binder resin are hydrophobic binder resins, more preferably phenolic resins e.g. novolacs and vinyl phenols.

[0041] The IR-dyes are present preferably in an amount between 10 and 80 parts by weight of the total amount of said IR-sensitive top layer.

[0042] The total amount of the top layer preferably ranges from 0.1 to 10 g/m<sup>2</sup> more preferably from 0.3 to 2 g/m<sup>2</sup>.

[0043] In the top layer a difference in the capacity of being penetrated and/or solubilised by the aqueous alkaline solution is generated upon image-wise exposure according to the invention.

[0044] In the present invention the said capacity is increased upon image-wise IR exposure to such degree that the imaged parts of the top layer and the underlying areas of the first layer will be cleaned out during development without solubilising and/or damaging the non-imaged parts.

[0045] The development with the aqueous alkaline solution is preferably done within an interval of 5 to 120 seconds.

[0046] Between the top layer and the lithographic base the present invention comprises a first layer soluble in an aqueous developing solution, more preferably an aqueous alkaline developing solution with a pH between 7.5 and 14. Said layer is preferably contiguous to the top layer. The alkali soluble polymers used in this layer are preferably hydro-

phobic and ink accepting polymers as used in conventional positive or negative working PS-plates e.g. novolac, polyvinyl phenols, carboxy substituted polymers etc. Typical examples of these polymers are described in DE-A- 4 007 428, DE-A- 4 027 301 and DE-A- 4 445 820. The hydrophobic polymer used in connection with the present invention is further characterised by insolubility in water and at least partial solubility/swellability in an alkaline solution and/or at least partial solubility in water when combined with a cosolvent. Furthermore this aqueous alkali soluble layer is preferably a visible light- and UV-light desensitised layer. Said layer is preferably thermally hardenable. This preferably visible light- or UV-light desensitised layer does not comprise photosensitive ingredients such as diazo compounds, photoacids, photoinitiators, quinone diazides, sensitizers etc. which absorb in the wavelength range of 250nm to 650nm. In this way a daylight stable printing plate can be obtained. Said first layer preferably also includes a low molecular acid, preferably a carboxylic acid, still more preferably a benzoic acid, most preferably 3,4,5-trimethoxybenzoic acid.

[0047] The ratio between the total amount of low molecular acid and polymer in the first layer preferably ranges from 2:98 to 40:60, more preferably from 5:95 to 20:80. The total amount of said first layer preferably ranges from 0.1 to 10 g/m<sup>2</sup>, more preferably from 0.3 to 2 g/m<sup>2</sup>.

[0048] In the imaging element according to the present invention, the lithographic base can be an anodised aluminum. A particularly preferred lithographic base is an electrochemically grained and anodised aluminum support. The anodised aluminum support may be treated to improve the hydrophilic properties of its surface. For example, the aluminum support may be silicated by treating its surface with sodium silicate solution at elevated temperature, e.g. 95°C. Alternatively, a phosphate treatment may be applied which involves treating the aluminum oxide surface with a phosphate solution that may further contain an inorganic fluoride. Further, the aluminum oxide surface may be rinsed with a citric acid or citrate solution. This treatment may be carried out at room temperature or can be carried out at a slightly elevated temperature of about 30 to 50°C. A further interesting treatment involves rinsing the aluminum oxide surface with a bicarbonated solution. Still further, the aluminum oxide surface may be treated with polyvinylphosphonic acid, polyvinylmethylphosphonic acid, phosphoric acid esters of polyvinyl alcohol, polyvinylsulphonic acid, polyvinylbenzenesulphonic acid, sulphuric acid esters of polyvinyl alcohol, and acetals of polyvinyl alcohols formed by reaction with a sulphonated aliphatic aldehyde. It is further evident that one or more of these post treatments may be carried out alone or in combination. More detailed descriptions of these treatments are given in GB-A- 1 084 070, DE-A- 4 423 140, DE-A- 4 417 907, EP-A- 659 909, EP-A- 537 633, DE-A- 4 001 466, EP-A- 292 801, EP-A- 291 760 and US-P- 4 458 005.

[0049] According to another embodiment in connection with the present invention, the lithographic base having a hydrophilic surface comprises a flexible support, such as e.g. paper or plastic film, provided with a cross-linked hydrophilic layer. A particularly suitable cross-linked hydrophilic layer may be obtained from a hydrophilic binder cross-linked with a cross-linking agent such as formaldehyde, glyoxal, polyisocyanate or a hydrolysed tetraalkylorthosilicate. The latter is particularly preferred.

[0050] As hydrophilic binder there may be used hydrophilic (co)polymers such as for example, homopolymers and copolymers of vinyl alcohol, acrylamide, methylol acrylamide, methylol methacrylamide, acrylic acid, methacrylic acid, hydroxyethyl acrylate, hydroxyethyl methacrylate or maleic anhydride/vinylmethylether copolymers. The hydrophilicity of the (co)polymer or (co)polymer mixture used is preferably the same as or higher than the hydrophilicity of polyvinyl acetate hydrolyzed to at least an extent of 60 percent by weight, preferably 80 percent by weight.

[0051] The amount of crosslinking agent, in particular of tetraalkyl orthosilicate, is preferably at least 0.2 parts by weight per part by weight of hydrophilic binder, more preferably between 0.5 and 5 parts by weight, most preferably between 1.0 parts by weight and 3 parts by weight.

[0052] A cross-linked hydrophilic layer in a lithographic base used in accordance with the present embodiment preferably also contains substances that increase the mechanical strength and the porosity of the layer. For this purpose colloidal silica may be used. The colloidal silica employed may be in the form of any commercially available water-dispersion of colloidal silica for example having an average particle size up to 40 nm, e.g. 20 nm. In addition inert particles of larger size than the colloidal silica can be added e.g. silica prepared according to Stöber as described in J. Colloid and Interface Sci., Vol. 26, 1968, pages 62 to 69 or alumina particles or particles having an average diameter of at least 100 nm which are particles of titanium dioxide or other heavy metal oxides. By incorporating these particles the surface of the cross-linked hydrophilic layer is given a uniform rough texture consisting of microscopic hills and valleys, which serve as storage places for water in background areas.

[0053] The thickness of a cross-linked hydrophilic layer in a lithographic base in accordance with this embodiment may vary in the range of 0.2 to 25 µm and is preferably 1 to 10 µm.

[0054] Particular examples of suitable cross-linked hydrophilic layers for use in accordance with the present invention are disclosed in EP-A- 601 240, GB-P- 1 419 512, FR-P- 2 300 354, US-P- 3 971 660, US-P- 4 284 705 and EP-A- 514 490.

[0055] As flexible support of a lithographic base in connection with the present embodiment it is particularly preferred to use a plastic film e.g. substrated polyethylene terephthalate film, cellulose acetate film, polystyrene film, polycarbonate film etc... The plastic film support may be opaque or transparent.

[0056] It is particularly preferred to use a polyester film support to which an adhesion improving layer has been pro-

vided. Particularly suitable adhesion improving layers for use in accordance with the present invention comprise a hydrophilic binder and colloidal silica as disclosed in EP-A- 619 524, EP-A- 620 502 and EP-A- 619 525. Preferably, the amount of silica in the adhesion improving layer is between 200 mg per m<sup>2</sup> and 750 mg per m<sup>2</sup>. Further, the ratio of silica to hydrophilic binder is preferably more than 1 and the surface area of the colloidal silica is preferably at least 300 m<sup>2</sup> per gram, more preferably at least 500 m<sup>2</sup> per gram.

[0057] Image-wise exposure in connection with the present invention is an image-wise scanning exposure involving the use of a laser that operates in the infrared or near-infrared, i.e. wavelength range of 700-1500 nm. Most preferred are laser diodes emitting in the near-infrared. Exposure of the imaging element can be performed with lasers with a short as well as with lasers with a long pixel dwell time. Preferred are lasers with a pixel dwell time between 0.005 µs and 20 µs.

[0058] After the image-wise exposure the heat mode imaging element is developed by rinsing it with an aqueous alkaline solution. The aqueous alkaline solutions used in the present invention are those that are used for developing conventional positive working presensitised printing plates and have preferably a pH between 11.5 and 14. Thus the imaged parts of the top layer that were rendered more penetrable for the aqueous alkaline solution upon exposure and the corresponding parts of the underlying layer are cleaned-out whereby a positive working printing plate is obtained.

[0059] In the present invention, the composition of the developer used is also very important.

[0060] Therefore, to perform development processing stably for a long time period particularly important are qualities such as strength of alkali and the concentration of silicates in the developer. Under such circumstances, the present inventors have found that a rapid high temperature processing can be performed, that the amount of the replenisher to be supplemented is low and that a stable development processing can be performed over a long time period of the order of not less than 3 months without exchanging the developer only when the developer having the foregoing composition is used.

[0061] The developers and replenishers for developer used in the invention are preferably aqueous solutions mainly composed of alkali metal silicates and alkali metal hydroxides represented by MOH or their oxyde, represented by M<sub>2</sub>O, wherein said developer contains SiO<sub>2</sub> and M<sub>2</sub>O in a molar ratio of 0.5 to 1.5 and a concentration of SiO<sub>2</sub> of 0.5 to 5% by weight. As such alkali metal silicates, preferably used are, for instance, sodium silicate, potassium silicate, lithium silicate and sodium metasilicate. On the other hand, as such alkali metal hydroxides, preferred are sodium hydroxide, potassium hydroxide and lithium hydroxide.

[0062] The developers used in the invention may simultaneously contain other alkaline agents. Examples of such other alkaline agents include such inorganic alkaline agents as ammonium hydroxide, sodium tertiary phosphate, sodium secondary phosphate, potassium tertiary phosphate, potassium secondary phosphate, ammonium tertiary phosphate, ammonium secondary phosphate, sodium bicarbonate, sodium carbonate, potassium carbonate and ammonium carbonate; and such organic alkaline agents as mono-, di- or triethanolamine, mono-, di- or trimethylamine, mono-, di- or triethylamine, mono- or di-isopropylamine, n-butylamine, mono-, di- or triisopropanolamine, ethyleneimine, ethylenediamine and tetramethylammonium hydroxide.

[0063] In the present invention, particularly important is the molar ratio in the developer of [SiO<sub>2</sub>] / [M<sub>2</sub>O], which is generally 0.6 to 1.5, preferably 0.7 to 1.3. This is because if the molar ratio is less than 0.6, great scattering of activity is observed, while if it exceeds 1.5, it becomes difficult to perform rapid development and the dissolving out or removal of the light-sensitive layer on non-image areas is liable to be incomplete. In addition, the concentration of SiO<sub>2</sub> in the developer and replenisher preferably ranges from 1 to 4 % by weight. Such limitation of the concentration of SiO<sub>2</sub> makes it possible to stably provide lithographic printing plates having good finishing qualities even when a large amount of plates according to the invention are processed for a long time period.

[0064] In a particular preferred embodiment, an aqueous solution of an alkali metal silicate having a molar ratio [SiO<sub>2</sub>] / [M<sub>2</sub>O], which ranges from 1.0 to 1.5 and a concentration of SiO<sub>2</sub> of 1 to 4 % by weight is used as a developer. In such case, it is a matter of course that a replenisher having alkali strength equal to or more than that of the developer is employed. In order to decrease the amount of the replenisher to be supplied, it is advantageous that a molar ratio, [SiO<sub>2</sub>] / [M<sub>2</sub>O], of the replenisher is equal to or smaller than that of the developer, or that a concentration of SiO<sub>2</sub> is high if the molar ratio of the developer is equal to that of the replenisher.

[0065] In the developers and the replenishers used in the invention, it is possible to simultaneously use organic solvents having solubility in water at 20 °C of not more than 10 % by weight according to need. Examples of such organic solvents are such carboxilic acid esters as ethyl acetate, propyl acetate, butyl acetate, amyl acetate, benzyl acetate, ethylene glycol monobutyl acetate, butyl lactate and butyl levulinate; such ketones as ethyl butyl ketone, methyl isobutyl ketone and cyclohexanone; such alcohols as ethylene glycol monobutyl ether, ethylene glycol benzyl ether, ethylene glycol monophenyl ether, benzyl alcohol, methylphenylcarbinol, n-amyl alcohol and methylamyl alcohol; such alkyl-substituted aromatic hydrocarbons as xylene; and such halogenated hydrocarbons as methylene dichloride and monochlorobenzene. These organic solvents may be used alone or in combination. Particularly preferred is benzyl alcohol in the invention. These organic solvents are added to the developer or replenisher therefor generally in an amount of not more than 5 % by weight and preferably not more than 4 % by weight.

[0066] The developers and replenishers used in the present invention may simultaneously contain a surfactant for the purpose of improving developing properties thereof. Examples of such surfactants include salts of higher alcohol (C8 ~ C22) sulfuric acid esters such as sodium salt of lauryl alcohol sulfate, sodium salt of octyl alcohol sulfate, ammonium salt of lauryl alcohol sulfate, Teepol B-81 (trade mark, available from Shell Chemicals Co., Ltd.) and disodium alkyl sulfates; salts of aliphatic alcohol phosphoric acid esters such as sodium salt of cetyl alcohol phosphate; alkyl aryl sulfonic acid salts such as sodium salt of dodecylbenzene sulfonate, sodium salt of isopropyl naphthalene sulfonate, sodium salt of dinaphthalene disulfonate and sodium salt of metanitrobenzene sulfonate; sulfonic acid salts of alkylamides such as C<sub>17</sub>H<sub>33</sub>CON(CH<sub>3</sub>)CH<sub>2</sub>CH<sub>2</sub>SO<sub>3</sub>Na and sulfonic acid salts of dibasic aliphatic acid esters such as sodium dioctyl sulfosuccinate and sodium dihexyl sulfosuccinate. These surfactants may be used alone or in combination. Particularly preferred are sulfonic acid salts. These surfactants may be used in an amount of generally not more than 5 % by weight and preferably not more than 3 % by weight.

[0067] In order to enhance developing stability of the developers and replenishers used in the invention, the following compounds may simultaneously be used.

[0068] Examples of such compounds are neutral salts such as NaCl, KCl and KBr as disclosed in JN-A- 58- 75 152; chelating agents such as EDTA and NTA as disclosed in JN-A- 58- 190 952 (U.S-A- 4 469 776), complexes such as [Co(NH<sub>3</sub>)<sub>6</sub>]Cl<sub>3</sub> as disclosed in JN-A- 59- 121 336 (US-A- 4 606 995); ionizable compounds of elements of the group IIa, IIIa or IIIb of the Periodic Table such as those disclosed in JN-A- 55- 25 100; anionic or amphoteric surfactants such as sodium alkyl naphthalene sulfonate and N-tetradecyl-N,N-dihydroxyethyl betaine as disclosed in JN-A- 50- 51 324; tetramethyldecyne diol as disclosed in US-A- 4 374 920; non-ionic surfactants as disclosed in JN-A- 60- 213 943; cat-ionic polymers such as methyl chloride quaternary products of p-dimethylaminomethyl polystyrene as disclosed in JN-A- 55- 95 946; amphoteric polyelectrolytes such as copolymer of vinylbenzyl trimethylammonium chloride and sodium acrylate as disclosed in JN-A- 56- 142 528; reducing inorganic salts such as sodium sulfite as disclosed in JN-A- 57- 192 952 (US-A- 4 467 027) and alkaline-soluble mercapto compounds or thioether compounds such as thiosalicylic acid, cysteine and thioglycolic acid; inorganic lithium compounds such as lithium chloride as disclosed in JN-A- 58- 59 444; organic lithium compounds such as lithium benzoate as disclosed in JN-A- 50 34 442; organometallic surfactants containing Si, Ti or the like as disclosed in JN-A- 59- 75 255; organoboron compounds as disclosed in JN-A- 59- 84 241 (US-A- 4 500 625); quaternary ammonium salts such as tetraalkylammonium oxides as disclosed in EP-A- 101 010; and bactericides such as sodium dehydroacetate as disclosed in JN-A- 63- 226 657.

In the method for development processing of the present invention, any known means of supplementing a replenisher for developer may be employed. Examples of such methods preferably used are a method for intermittently or continuously supplementing a replenisher as a function of the amount of PS plates processed and time as disclosed in JN-A- 55- 115 039 (GB-A- 2 046 931), a method comprising disposing a sensor for detecting the degree of light-sensitive layer dissolved out in the middle portion of a developing zone and supplementing the replenisher in proportion to the detected degree of the light-sensitive layer dissolved out as disclosed in JN-A- 58- 95 349 (US-A- 4 537 496); a method comprising determining the impedance value of a developer and processing the detected impedance value by a computer to perform supplementation of a replenisher as disclosed in GB-A- 2 208 249.

[0069] The printing plate of the present invention can also be used in the printing process as a seamless sleeve printing plate. In this option the printing plate is soldered in a cylindrical form by means of a laser. This cylindrical printing plate which has as diameter the diameter of the print cylinder is slid on the print cylinder instead of applying in a classical way a classically formed printing plate. More details on sleeves are given in "Grafisch Nieuws" ed. Keesing, 15, 1995, page 4 to 6.

[0070] After the development of an image-wise exposed imaging element with an aqueous alkaline solution and drying, the obtained plate can be used as a printing plate as such. However, to improve durability it is still possible to bake said plate at a temperature between 200°C and 300°C for a period of 30 seconds to 5 minutes. Also the imaging element can be subjected to an overall post-exposure to UV-radiation to harden the image in order to increase the run length of the printing plate.

[0071] The following examples illustrate the present invention without limiting it thereto. All parts and percentages are by weight unless otherwise specified.

## 50 EXAMPLES

EXAMPLE 1 :Positive working thermal plate based on an alkali-soluble binder.

Preparation of the lithographic base

[0072] A 0.20 mm thick aluminum foil was degreased by immersing the foil in an aqueous solution containing 5 g/l of sodium hydroxide at 50°C and rinsed with demineralized water. The foil was then electrochemically grained using an alternating current in an aqueous solution containing 4 g/l of hydrochloric acid, 4 g/l of hydroboric acid and 5 g/l of alu-

minimum ions at a temperature of 35°C and a current density of 1200 A/m<sup>2</sup> to form a surface topography with an average center-line roughness Ra of 0.5 mm.

[0073] After rinsing with demineralized water the aluminum foil was then etched with an aqueous solution containing 300 g/l of sulfuric acid at 60°C for 180 seconds and rinsed with demineralized water at 25°C for 30 seconds.

[0074] The foil was subsequently subjected to anodic oxidation in an aqueous solution containing 200 g/l of sulfuric acid at a temperature of 45°C, a voltage of about 10 V and a current density of 150 A/m<sup>2</sup> for about 300 seconds to form an anodic oxidation film of 3.00 g/m<sup>2</sup> of Al<sub>2</sub>O<sub>3</sub> then washed with demineralized water, posttreated with a solution containing polyvinylphosphonic acid and then with a solution containing aluminum trichloride, subsequently rinsed with demineralized water at 20°C during 120 seconds and dried.

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Preparation of the first layer.

[0075] To 484 g of tetrahydroturan and 288 g of methoxypropanol was added a solution of 72.6 g alnovol in 111.7 g of methoxypropanol and 9.86 g of 3,4,5-trimethoxybenzoic acid and said solution was coated on the anodized layer of the aluminum support at a wet thickness of 14 µm, giving a dry weight of 1.12 g/m<sup>2</sup>.

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Preparation of the top layer

[0076] To 28.66 g of tetrahydrofuran and 19.11 g of methoxypropanol was added a solution of 0.291 g novolac in 0.43 g of methoxypropanol and 0.291 g of IRD No 17 and said solution was coated at 30 µm wet thickness, giving a dry weight of 0.31 g/m<sup>2</sup>.

This material was imaged with a GERBER C42T™ internal drum platesetter at 12,000 rpm and 2540 dpi. The power level of the laser in the image plane was 6.65 W. After IR-exposure no layer damage, as a result of ablation, could be observed. This was also verified by measuring the optical density of the layer prior and after the IR-laser exposure (see table 1).

After exposure the material was developed in an alkaline developing solution (EP 26 developer commercially available from Agfa), dissolving very rapidly the IR-exposed areas, resulting in a positive working plate.

The plate was printed on a Heidelberg GTO46 printing machine with a conventional ink (K+E) and fountain solution (Rotamatic), resulting in good prints, i.e. no scumming in IR-exposed areas and good ink-uptake in the non-exposed areas.

COMPARATIVE EXAMPLE :Positive working thermal plate based on an alkali-soluble binder.

[0077] The lithographic base and the first layer were prepared and coated as described in example 1. The IR-sensitive top layer was coated from a 1.00% carbon black dispersion (SPECIAL SCHWARZ 250™) in methylethylketone/methoxypropanol 70/30 at 20 µm wet coating thickness. This material was imaged with a GERBER C42T™ internal drum platesetter at 12,000 rpm and 2540 dpi. The power level of the laser in the image plane was 3.5 W. After IR-exposure the top layer is clearly damaged by the IR-laser exposure, even at lower IR-laser power (3.5 W versus 6.65 W for example 1) as a result of ablation processes. On the surface of the layer small dust particles can be observed. This ablation was also quantified by measuring the optical density of the layer prior and after the IR-laser exposure (see table 1).

After exposure the material was developed in an alkaline developing solution (85% EP 26 developer commercially available from Agfa), dissolving very rapidly the IR-exposed areas, resulting in a positive working plate.

The plate was printed on a Heidelberg GTO46 printing machine with a conventional ink (K+E) and fountain solution (Rotamatic), resulting in good prints, i.e. no scumming in IR-exposed areas and good ink-uptake in the non-exposed areas.

EXAMPLE 2 :Positive working thermal plate based on an alkali-soluble binder.

[0078] The lithographic base and the first layer were prepared and coated as described in example 1.

Preparation of the top layer

[0079] To 28.66 g of tetrahydrofuran and 19.11 g of methoxypropanol was added a solution of 0.47 g novolac in 0.82 g of methoxypropanol and 0.112 g of IRD No 17 and said solution was coated at 30 µm wet thickness, giving a dry weight of 0.31 g/m<sup>2</sup>.

[0080] This material was imaged with a GERBER C42T™ internal drum platesetter at 12,000 rpm and 2540 dpi. The power level of the laser in the image plane was 6.65 W. After IR-exposure no layer damage, as a result of ablation, could

be observed. This was also verified by measuring the optical density of the layer prior and after the IR-laser exposure (see table 1).

After exposure the material was developed in an alkaline developing solution (EP 26 developer commercially available from Agfa), dissolving very rapidly the IR-exposed areas, resulting in a positive working plate.

5 The plate was printed on a Heidelberg GTO46 printing machine with a conventional ink (K+E) and fountain solution (rotamatic), resulting in good prints, i.e. no scumming in IR-exposed areas and good ink-uptake in the non-exposed areas.

Table 1

Example	Power Gerber C42T	Density prior to exposure	Density after exposure
Example 1	6.65 W	0.34	0.34
Example 2	6.65 W	0.19	0.19
Comparative ex	3.5 W	1.19	1.09

### Claims

20 1. A method for making lithographic printing plates including the following steps

a) preparing a heat mode imaging element having on a lithographic base with a hydrophilic surface a first layer including a polymer, soluble in an aqueous alkaline solution and a top layer on the same side of the lithographic base as the first layer which top layer is sensitive to IR-radiation and is unpenetrable for an alkaline developer containing  $\text{SiO}_2$  as silicate;  
 25 b) exposing imagewise said heat mode imaging element to IR-radiation;  
 c) developing said imagewise exposed heat mode imaging element with said alkaline developer so that the exposed areas of the top layer and the underlying areas of the first layer are dissolved and the unexposed areas of the first layer remain undissolved characterized in that said top layer includes an IR-dye in an amount between 1 and 100% by weight of the total amount of said IR-sensitive top layer selected from the group consisting of indoaniline dyes, cyanine dyes, merocyanine dyes, oxonol dyes, porphine derivatives, anthraquinone dyes, merostyryl dyes, pyrylium compounds, diphenyl and triphenyl azo compounds and squarylium derivatives.

35 2. A method according to claim 1 for making lithographic printing plates including the following steps

a) preparing a heat mode imaging element having on a lithographic base with a hydrophilic surface a first layer including a polymer, soluble in an aqueous alkaline solution and a top layer on the same side of the lithographic base as the first layer which top layer consist of a binder resin, is sensitive to IR-radiation and is unpenetrable for an alkaline developer containing  $\text{SiO}_2$  as silicate;  
 40 b) exposing imagewise said heat mode imaging element to IR-radiation;  
 c) developing said imagewise exposed heat mode imaging element with said alkaline developer so that the exposed areas of the top layer and the underlying areas of the first layer are dissolved and the unexposed areas of the first layer remain undissolved characterized in that said top layer includes an IR-dye in an amount between 1 and 100% by weight of the total amount of said IR-sensitive top layer selected from the group consisting of indoaniline dyes, cyanine dyes, merocyanine dyes, oxonol dyes, porphine derivatives, anthraquinone dyes, merostyryl dyes, pyrylium compounds, diphenyl and triphenyl azo compounds and squarylium derivatives.

50 3. A method for making lithographic printing plates according to claim 2 wherein said binder resin is a novolac or a hydroxystyrene containing polymer.

4. A method for making lithographic printing plates according to any of claims 1 to 3 wherein said polymer included in the first layer is a hydrophobic polymer.

55 5. A method for making lithographic printing plates according to any of claims 1 to 4 wherein said polymer included in the first layer is a novolac or a hydroxystyrene containing polymer.

6. A method for making lithographic printing plates according to any of claims 1 to 5 wherein said first layer includes a low molecular acid
- 5 7. A method for making lithographic printing plates according to any of claims 1 to 6 wherein said first layer is a visible light- and UV light- desensitized layer.
8. A method for making lithographic printing plates according to any of claims 1 to 7 wherein said first layer is thermally hardenable.
- 10 9. A method for making lithographic printing plates according to any of claims 1 to 8 wherein said lithographic base having a hydrophilic surface is an electrochemically grained and anodized aluminum support.
- 15 10. A method for making lithographic printing plates according to claim 9 wherein said aluminum support is treated with polyvinylphosphonic acid.
11. A method for making lithographic printing plates according to any of claims 1 to 10 wherein said alkaline developer comprises  $\text{SiO}_2$  and  $\text{M}_2\text{O}$  in a molar ratio of 0.5 to 1.5 and a concentration of  $\text{SiO}_2$  of 0.5 to 5% by weight.

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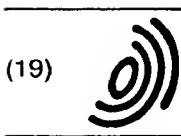
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### (54) A method for making positive printing plates from a heat mode sensitive imaging element

(57) According to the present invention there is provided a method for making lithographic printing plates including the following steps

- a) preparing a heat mode imaging element having on a lithographic base with a hydrophilic surface a first layer including a polymer, soluble in an aqueous alkaline solution and a top layer on the same side of the lithographic base as the first layer which top layer is sensitive to IR-radiation and is unpene- trable for an alkaline developer containing SiO<sub>2</sub> as silicates;
- b) exposing imagewise said heat mode imaging element to IR-radiation;
- c) developing said imagewise exposed heat mode imaging element with said alkaline developer so that the exposed areas of the top layer and the underlying areas of the first layer are dissolved and the unexposed areas of the first layer remain undis- solved characterized in that said top layer includes an IR-dye in an amount between 1 and 100% by weight of the total amount of said IR-sensitive top layer selected from the group consisting of indoaniline dyes, cyanine dyes, merocyanine dyes, oxonol dyes, porphine derivatives, anthraquinone dyes, merostyryl dyes, pyrylium compounds, diphe- nyl and triphenyl azo compounds and squarylium derivatives.



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## EUROPEAN SEARCH REPORT

Application Number

EP 98 20 3122

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
X	GB 1 245 924 A (AGFA-GEVAERT N.V.) 15 September 1971 (1971-09-15)	1-11	B41C1/10 B41M5/36
Y	* page 5, line 61 - page 5, line 62 * * page 1, line 63 * * page 2, line 2 - line 10 * * page 2, line 72 - line 78 * * page 6, line 35 - line 53; example 8 * * page 5, line 33 - page 6, line 75 * ---	1-11	
Y	US 5 466 557 A (HALEY NEIL F ET AL) 14 November 1995 (1995-11-14)	1-11	
Y	* column 8, line 50 - line 51 * * column 10, line 48 - line 56; claim 1 * ---	1-11	
Y	US 5 491 046 A (HALEY NEIL F ET AL) 13 February 1996 (1996-02-13) * column 9, line 1 - line 3 * * column 9, line 28 * ---	1,6	
D,Y	DE 43 31 162 A (BAYER AG) 16 March 1995 (1995-03-16) * the formulae * * page 13, line 36 - line 39 * ---	1	TECHNICAL FIELDS SEARCHED (Int.Cl.6)
Y	EP 0 706 899 A (AGFA GEVAERT NV) 17 April 1996 (1996-04-17) * page 11 * ---	1	B41C B41M G03F
Y	EP 0 366 461 A (JUJO PAPER CO LTD) 2 May 1990 (1990-05-02) * the formulae * ---	1	
Y	WO 95 07822 A (AGFA GEVAERT NV ;UYTTERHOEVEN HERMAN (BE); BASTIAENS LUC (BE); ACK) 23 March 1995 (1995-03-23) * the formulae * ---	1	
		-/-	
The present search report has been drawn up for all claims			
Place of search	Date of completion of the search	Examiner	
THE HAGUE	4 November 1999	Rasschaert, A	
CATEGORY OF CITED DOCUMENTS			
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## EUROPEAN SEARCH REPORT

Application Number  
EP 98 20 3122

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
Y	EP 0 573 092 A (AGFA GEVAERT NV) 8 December 1993 (1993-12-08) * page 3, line 22 - line 36; claims 1,10 * ---	1	
Y	EP 0 347 245 A (FUJI PHOTO FILM CO LTD) 20 December 1989 (1989-12-20) * the whole document * ---	1-11	
Y	GB 1 160 221 A (GEVAERT-AGFA N.V.) 6 August 1969 (1969-08-06) * page 6, line 55 - line 60 * ---	1	
Y	GB 1 076 799 A (AGFA A.G.) * claim 6 * ---	1	
A	GB 1 155 035 A (GEVAERT-AGFA N.V.) 11 June 1969 (1969-06-11) * claim 10 * * page 4, line 41 - line 47 * * page 3, line 27 * * page 2, line 18 - page 3, line 13 * ---	1	
A	GB 1 154 568 A (AGFA-GEVAERT N.V.) 11 June 1969 (1969-06-11) * the whole document * ---	1	
A	EP 0 732 628 A (MINNESOTA MINING & MFG) 18 September 1996 (1996-09-18) * the whole document * -----	1	
The present search report has been drawn up for all claims			
Place of search		Date of completion of the search	
THE HAGUE		4 November 1999	
Examiner		Rasschaert, A	
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document			
T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

ANNEX TO THE EUROPEAN SEARCH REPORT  
ON EUROPEAN PATENT APPLICATION NO.

EP 98 20 3122

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on. The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

04-11-1999

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
GB 1245924	A	15-09-1971	BE 721468 A DE 1797415 A FR 1588977 A US 3628953 A	27-03-1969 19-08-1971 16-03-1970 21-12-1971
US 5466557	A	14-11-1995	NONE	
US 5491046	A	13-02-1996	NONE	
DE 4331162	A	16-03-1995	DE 69412495 D DE 69412495 T DE 69415544 D DE 69415544 T WO 9507950 A WO 9507822 A EP 0719217 A EP 0719304 A JP 9502477 T JP 9504239 T US 5948600 A	17-09-1998 25-03-1999 04-02-1999 26-08-1999 23-03-1995 23-03-1995 03-07-1996 03-07-1996 11-03-1997 28-04-1997 07-09-1999
EP 0706899	A	17-04-1996	US 5506085 A	09-04-1996
EP 0366461	A	02-05-1990	JP 2120082 A JP 2530697 B DE 68927780 D DE 68927780 T US 5075146 A	08-05-1990 04-09-1996 27-03-1997 28-08-1997 24-12-1991
WO 9507822	A	23-03-1995	DE 4331162 A DE 69412495 D DE 69412495 T DE 69415544 D DE 69415544 T WO 9507950 A EP 0719217 A EP 0719304 A JP 9502477 T JP 9504239 T US 5948600 A	16-03-1995 17-09-1998 25-03-1999 04-02-1999 26-08-1999 23-03-1995 03-07-1996 03-07-1996 11-03-1997 28-04-1997 07-09-1999
EP 0573092	A	08-12-1993	JP 6055869 A	01-03-1994
EP 0347245	A	20-12-1989	JP 2003065 A JP 2639693 B DE 68922144 D	08-01-1990 13-08-1997 18-05-1995

ANNEX TO THE EUROPEAN SEARCH REPORT  
ON EUROPEAN PATENT APPLICATION NO.

EP 98 20 3122

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on. The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

04-11-1999

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
EP 0347245 A		DE	68922144 T	10-08-1995
GB 1160221 A	06-08-1969	AT	279350 B	10-03-1970
		BE	681138 A	17-11-1966
		CH	480189 A	31-10-1969
		DE	1571816 A	14-01-1971
		FR	1532243 A	18-11-1968
		NL	6606719 A	25-10-1966
		SE	338712 B	13-09-1971
		US	3793025 A	19-02-1974
		US	4004924 A	25-01-1977
GB 1076799 A		BE	657502 A	23-06-1965
		DE	1447572 A	05-12-1968
		FR	1417929 A	09-02-1966
GB 1155035 A	11-06-1969	NL	6608712 A	25-11-1966
GB 1154568 A	11-06-1969	US	3811773 A	21-05-1974
		BE	683054 A	27-11-1966
		CH	477295 A	31-08-1969
		NL	6608711 A	25-11-1974
EP 0732628 A	18-09-1996	JP	8262742 A	11-10-1996
		US	5670294 A	23-09-1997